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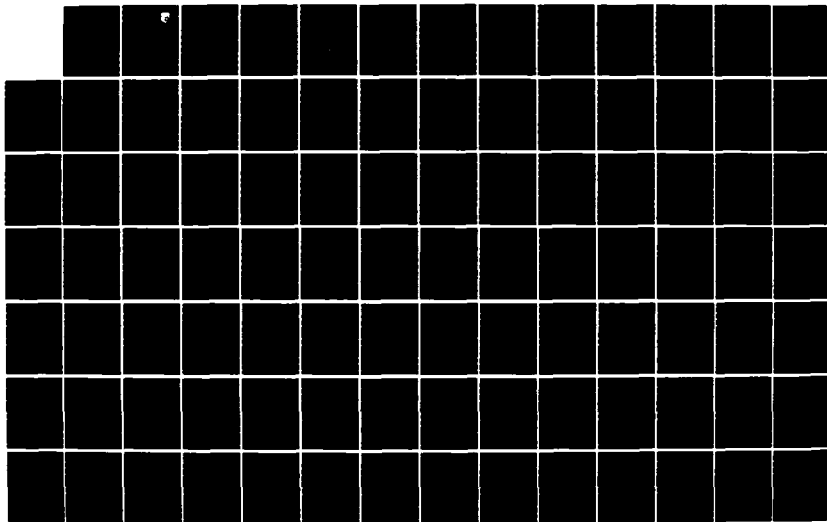   WRIGHT-PATTERSON AFB OH   W Z STRANG SEP 86
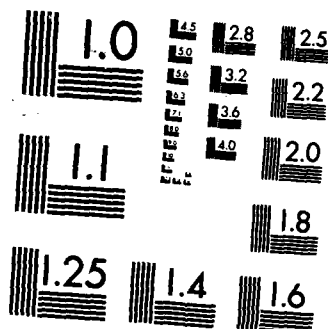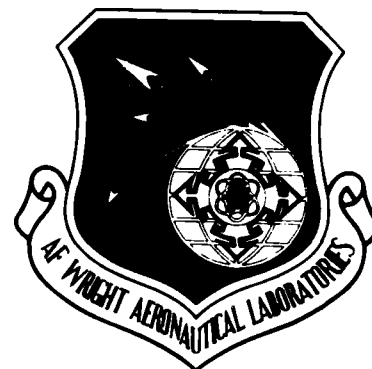UNCLASSIFIED   AFWAL-TR-86-3085   F/G 20/13   NL

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A KINETIC THEORY DEVELOPMENT OF THE EQUATIONS OF
MOTION OF A DIATOMIC GAS

William Z. Strang, First Lieutenant, USAF
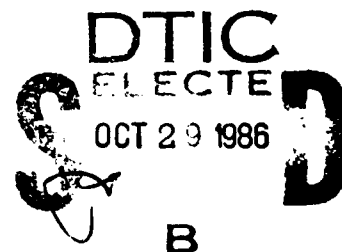Aerodynamics and Airframe Branch
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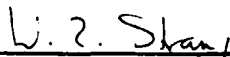WRIGHT-PATTERSON AIR FORCE BASE, OHIO   45433-6553

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The Liouville equation is solved for a diatomic gas in molecular chaos. Modelling the gas molecule as a rigid rotor yields a Boltzmann-type equation in eleven independent variables. Applying Enskog's expansion method of solution to the Boltzmann-type equation and substituting the first two terms of the distribution function expansion into conservation equations produces the equivalent of the Navier-Stokes equations in five space. The resulting stress tensor predicts the development of periodic stresses approximately ten orders of magnitude smaller than the shear stresses. Other predictions agree closely with experiment and statistical thermodynamics. Keywords: Statistical Mechanics,

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FOREWORD

This report was prepared by William Z. Strang of the Aerodynamics and Airframe Branch, Aeromechanics Division, Flight Dynamics Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson AFB, Ohio, under Project 2404, Aeromechanics Technology, Task 240410, Aerodynamics/Airframe Technology, Unit 240410A1, Aerodynamic and Design Analysis Methods.

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TABLE OF CONTENTS

LIST OF SYMBOLS

B_i = a value which when multiplied by the $i\underline{\text{th}}$ component of velocity produces the $i\underline{\text{th}}$ component of momentum

C_v = heat capacity at constant volume

C_p = heat capacity at constant pressure

Ψ = any molecular property that is a function of n, p_i, and T

δ_{ij} = Kronecker delta function

ε_{ijk} = Levi-Civita permutation function

$\hat{e}_i$ = unit vector in i-direction

f = distribution function

F_i = $i\underline{\text{th}}$ component of a generalized force or torque

$\vec{F}$ = generalized force or torque vector

γ = ratio of specific heats

H = Hamiltonian

I = moment of inertia

$\vec{J}$ = impulse vector

k = Boltzmann's constant

λ = coefficient of heat conductivity

m = mass

μ = coefficient of viscosity

n = molecular number density

N = number of molecules

p_i = $i\underline{\text{th}}$ component of molecular momentum

$\vec{p}$ = momentum vector of five dimensions

$\bar{p}_i$ = i^{th} component of average molecular momentum

P_i = i^{th} component of peculiar molecular momentum

p = thermodynamic pressure

q_i = i^{th} dimension in Euclidean space

$\vec{q}$ = position vector in a Euclidean five space

Q_j = heat flux in j-direction

r_g = molecular radius of gyration

ρ = density

t = time

T = temperature

τ_{ij} = stress tensor

$u, v, w, \dot{\theta}, \dot{\phi}$ = velocity components in each degree of freedom

$\vec{v}$ = linear velocity vector of three dimensions

$\vec{\omega}$ = angular velocity vector of two dimensions

V = volume

x, y, z, θ, ϕ = the five independent coordinates of a rigid rotor

$r, \beta, \varepsilon, \delta$ = the four independent variables specifying a collision geometry in a Euclidean five space

Z = partition function

Subscripts

c = quantity at collision

o = value at an initial time

R = relative

a = pertaining to molecule a

b = pertaining to molecule b

i, j, k = indices

Superscripts

$-$ = average quantity

$'$ = quantity after collision

^{o} = non-divergent quantity

$\rightarrow$ = vector quantity

γ = gas phase space

μ = molecule phase space

$\cdot$ = time derivative

s = symmetric tensor

SECTION I

INTRODUCTION

This paper presents a derivation of the equations of motion of a gas whose molecules may be modelled as rigid rotors. A rigid rotor has three translational degrees of freedom and two rotational degrees of freedom, but no provisions for vibration, electronic excitation, or nuclear excitation. At moderate temperatures, however, both quantum mechanics and statistical thermodynamics show the rigid rotor to be an excellent model of the diatomic gas molecule.

Beginning with the classical Liouville equation, the author develops a "Boltzmann-type equation" governing the motion of a rigid rotor. With the exception of four additional independent variables due to angular momentum and orientation, the Boltzmann-type equation is identical to the Boltzmann equation. The Boltzmann-type equation is solved via the Hilbert-Enskog-Chapman theory[1,2] for the first two terms of the expansion of the distribution function. The governing equations of motion of the gas are then derived by substituting those first two terms of the distribution function expansion into the conservation equations of mass, linear momentum, total angular momentum, and energy. The resulting equations of motion mimic the Navier-Stokes equations except with regard to the additional angular momentum conservation equations, the molecular constants, the heat flux vector, and the stress tensor.

The development of the Navier-Stokes equations from kinetic theory is based upon a smooth-sphere molecular model possessing three translational degrees of freedom only. Such a model is an excellent representation of monatomic gas molecules at moderate temperatures. The thermodynamic properties, i.e. equilibrium properties, of monatomic gases differ significantly from those of

the diatomic gases. Table 1 presents this difference and also the excellent comparison between experimental results and theoretical calculations based upon statistical thermodynamics and the above molecular models. One purpose of this study is to investigate whether weak non-equilibrium properties, i.e. flow properties, also strongly depend upon the gas type in question. If the flow properties do strongly depend on the gas type, the Navier-Stokes equations might be inaccurate when applied to some air flows. However, we shall see that this is not the case.

Another purpose of the current work is to introduce greater rigor into the development of the Boltzmann-type equation than had other workers[5,6,7] Kirkwood[8,9] paved the way in this regard; the present work merely specializes his development.

Some preliminary definitions and conventions are in order. The present work deals almost exclusively in a five-dimensional Euclidean space. A "surface" in this space is defined to be a four-dimensional geometry, while a "volume" is a five-dimensional geometry. Both vector and indicial notations are used in the present derivation. The specific selection of one notation over another is based upon the ease of interpretation. By convention, when the integrand is a function of the momentum, the integral limits are from negative infinity to positive infinity unless otherwise stated.

The governing equations of motion are next derived. Important results and notable assumptions are then summarized and the paper closes with a discussion and a short conclusion. Several mathematical developments appear in the appendices at the rear of the paper.

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Table 1. Molecular Constants

MONATOMIC GASES

	exp γ	calc γ	exp $Pr_{0^\circ C}$	calc $Pr_{0^\circ C}$	exp $S_{25^\circ C}$	calc $S_{25^\circ C}$
He	1.666	1.667	0.664	0.667	126.3	125.3
Ne	1.64	1.667	0.675	0.667	146.5	145.5
Ar	1.666	1.667	0.659	0.667	155.0	154.0
Kr	1.68	1.667	0.656	0.667	164.2	163.2
Xe	1.67	1.667	0.649	0.667	169.8	168.9

DIATOMIC GASES

	exp γ	calc γ	exp $Pr_{0^\circ C}$	calc $Pr_{0^\circ C}$	exp $S_{25^\circ C}$	calc $S_{25^\circ C}$
H_2	1.405	1.400	0.710	-----	130.7	129.7
HCl	1.39	1.400	0.881[*]	-----	186.2	186.0
N_2	1.405	1.400	0.722	-----	191.5	190.8
CO	1.402	1.400	0.745	-----	197.5	196.8
O_2	1.396	1.400	0.718	-----	205.1	195.1
Cl_2	1.35	1.400	0.771[*]	-----	223.0	219.8

[*] Experimental results at $25^\circ C$.

Entropy is in units of $J/^\circ K$-mole. Results gathered from Refs. 3 and 4.

SECTION II

DEVELOPMENT OF THE GOVERNING EQUATIONS OF MOTION

1. Derivation of the Boltzmann-type equation

The Liouville equation[2]

$$\frac{\mathcal{D}'f^{(N)}}{\mathcal{D}t} \equiv \frac{\partial\,{}^{\gamma}f^{(N)}}{\partial t} + \sum_{i=1}^{N}\left[\frac{\partial H}{\partial \vec{p}_i}\frac{\partial\,{}^{\gamma}f^{(N)}}{\partial \vec{q}_i} - \frac{\partial H}{\partial \vec{q}_i}\frac{\partial\,{}^{\gamma}f^{(N)}}{\partial \vec{p}_i}\right] = 0 \qquad 1$$

for the distribution function ${}^{\gamma}f^{(N)}(\vec{p}_N, \vec{q}_N, t)$ in the gas phase

space $(\vec{p}_N, \vec{q}_N)$ of systems of N molecules is the fundamental

equation of classical statistical mechanics. The Liouville

equation cannot generally be solved for ${}^{\gamma}f^{(N)}$. Fortunately, such

detailed information as that contained in

${}^{\gamma}f^{(N)}$ is not needed.

The present analysis shall be restricted to the first-order

distribution function, ${}^{\gamma}f_a^{(1)}$, of molecule a in the sub-phase space

$(\vec{p}_a, \vec{q}_a)$ of γ-space. Since,

$$\iint {}^{\gamma}f_a^{(1)}(\vec{q}_a, \vec{p}_a, t)\, d\vec{p}_a\, d\vec{q}_a = \iint {}^{\gamma}f^{(N)}(\vec{q}_N, \vec{p}_N, t)\, d\vec{p}_N\, d\vec{q}_N \qquad 2$$

the distribution function ${}^{\gamma}f_a^{(1)}$ is simply the integral of ${}^{\gamma}f^{(N)}$

over the sub phase space $(\vec{p}_\eta, \vec{q}_\eta)$ where η is the set of all

molecules exclusive of molecule a:

$$ {}^{\gamma}f_a^{(1)}(\vec{p}_a, \vec{q}_a, t) = \iint {}^{\gamma}f^{(N)}(\vec{p}_N, \vec{q}_N, t)\, d\vec{p}_\eta\, d\vec{q}_\eta \qquad 3$$

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provided such an integral is finite. This requires $^\gamma f^{(N)} \to 0$ sufficiently fast as $|\vec{p}|$, $|\vec{q}| \to \infty$. The Liouville equation in terms of $^\gamma f_a^{(1)}$ is thus

$$\frac{D\,^\gamma f_a^{(1)}}{Dt} = \frac{\partial\,^\gamma f_a^{(1)}}{\partial t} + \frac{\partial H}{\partial \vec{p}_a}\frac{\partial\,^\gamma f_a^{(1)}}{\partial \vec{q}_a} - \frac{\partial H}{\partial \vec{q}_a}\frac{\partial\,^\gamma f_a^{(1)}}{\partial \vec{p}_a} = 0. \qquad 4$$

The Liouville equation is next specialized to the case of a gas composed of rigid rotor molecules by substituting for the Hamiltonian of a rigid rotor. The Hamiltonian of a rigid rotor in an inertial reference frame is[3]:

$$H = \frac{1}{2m}\left[P_x^2 + P_y^2 + P_z^2 \right] + \frac{1}{2I}\left[P_\theta^2 + \frac{P_\phi^2}{\sin^2\theta} \right] + H^e + H^i \qquad 5$$

where x, y, and z are the Cartesian coordinates of the rotor's center of mass and θ, ϕ are the Euler angles of the rotor's orientation, such that

$$0 \leq \theta \leq \pi$$
$$0 \leq \phi \leq 2\pi.$$

H^e is the potential due to effects external to the gas. H^i, the intermolecular potential, is a function solely of the relative locations and orientations of the molecules. Substituting the rigid rotor Hamiltonian into equation four yields:

$$\frac{\partial\,^\gamma f_a^{(1)}}{\partial t} + \frac{P_{ia}}{B_{ia}}\frac{\partial\,^\gamma f_a^{(1)}}{\partial q_{ia}} + \vec{\mathcal{F}}_{ia}^e \frac{\partial\,^\gamma f_a^{(1)}}{\partial p_{ia}} + \vec{\mathcal{F}}_{ia}^i \frac{\partial\,^\gamma f_a^{(1)}}{\partial p_{ia}} + \frac{P_\phi^2 \cot\theta}{I \sin^2\theta}\frac{\partial\,^\gamma f_a^{(1)}}{\partial p_\theta} = 0 \qquad 6$$

where

$$j=1 \implies x\text{-direction}; \quad p_1 = mu; \quad B_1 = m$$
$$j=2 \implies y\text{-direction}; \quad p_2 = mv; \quad B_2 = m$$
$$j=3 \implies z\text{-direction}; \quad p_3 = mw; \quad B_3 = m$$
$$j=4 \implies \theta\text{-direction}; \quad p_4 = I\dot{\theta}; \quad B_4 = I$$
$$j=5 \implies \phi\text{-direction}; \quad p_5 = (I\sin^2\theta)\dot{\phi}; \quad B_5 = I\sin^2\theta$$

The last term of equation six represents a torque causing the rotor to precess from a general rotation to a rotation where θ is fixed at $\pi/2$. However, since the momental ellipsoid of a rotor is an infinitely long circular cylinder, the free rotation of a rigid rotor is stable. Therefore, this precessional term exists only in the presence of external torques. Such torques arise from both H^e and H^i. The present analysis shall be restricted to nonpolar molecules undergoing impulsive collisions so that the precessional term vanishes. Since nonpolar molecules are unaffected by external field torques, however, forces:

$$\tilde{f}_{4a}^e = \tilde{f}_{5a}^e = 0. \tag{7}$$

The above two assumptions lead to the equation:

$$\frac{\partial \, {}^r f_a^{(1)}}{\partial t} + \frac{p_{ja}}{B_{ja}} \frac{\partial \, {}^r f_a^{(1)}}{\partial q_{ja}} + \tilde{f}_{ja}^e \frac{\partial \, {}^r f_a^{(1)}}{\partial p_{ja}} + \tilde{f}_{ja}^i \frac{\partial \, {}^r f_a^{(1)}}{\partial p_{ja}} = 0. \tag{8}$$

Since

$$\tilde{f}_{ja}^i \neq \tilde{f}_{ja}^i (p_{ja}) \tag{9}$$

equation eight may be rewritten with the aid of equation two as:

$$\frac{\partial \, {}^r f_a^{(1)}}{\partial t} + \frac{p_{ja}}{B_{ja}} \frac{\partial \, {}^r f_a^{(1)}}{\partial q_{ja}} + \tilde{f}_{ja}^e \frac{\partial \, {}^r f_a^{(1)}}{\partial p_{ja}} = -\frac{\partial}{\partial p_{ja}} \iint \tilde{f}_{ja}^i \, {}^2 f^{(a)}(\vec{p}_n, \vec{q}_n, t) \, d\vec{p}_n \, d\vec{q}_n. \tag{10}$$

6

The right-hand term of equation 10 is the collision integral.
The collisional integral must be reduced to be a function of
$f_a^{(1)}$. Appendix A follows Kirkwood's work[8,9] for the reduction.
By assuming the gas to be dilute and in molecular chaos, we find
equation 10 to be equal to:

$$\frac{\partial \bar{f}_a}{\partial t} + \frac{P_{j\alpha}}{B_{j\alpha}} \frac{\partial \bar{f}_a}{\partial q_{j\alpha}} + \tilde{\mathcal{F}}_{j\alpha}^e \frac{\partial \bar{f}_a}{\partial P_{j\alpha}} = \frac{1}{\tau} \iint (\bar{f}_a' \bar{f}_b' - \bar{f}_a \bar{f}_b) \, d\vec{P}_b \, d\vec{q}_R \qquad 11$$

where:

$$\bar{f}_a = \bar{f}_a(\vec{P}_a, \vec{q}_a, t) \qquad\qquad \bar{f}_a' = \bar{f}_a'(\vec{P}_a - \vec{\Delta p}(\tau), \vec{q}_a, t)$$

$$\bar{f}_b = \bar{f}_b(\vec{P}_b, \vec{q}_b, t) \qquad\qquad \bar{f}_b' = \bar{f}_b'(\vec{P}_b + \vec{\Delta p}(\tau), \vec{q}_b, t) \qquad 12$$

and where τ is a characteristic time long in comparison to the
duration of a collision but short in comparison to a Poincaré
cycle[8].

Appendix B develops the actual equations of motion governing
binary collisions between rigid rotors. For any given direct
collision between impulsively colliding rigid rotors, we see that
there exists an inverse collision. The existence of inverse
collisions is of crucial importance to the present work.
Boltzmann's H-Theorem[1] may be shown to hold for rigid rotors and
the relation

$$dp_a dp_b = dp_a' dp_b' \qquad 13$$

holds.

The relative spatial coordinate, $\vec{q}_R$, deserves further
consideration. The coordinate is a five-space volume. Only the

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portion of five space in which a type b molecule is able to
collide with a type a molecule within time τ contributes to the
collision integral. This portion of five space may be considered
as a five-space cylinder with the generator $|\vec{V}_R|$. The vector,
$\vec{V}_R$, is the relative velocity of the points of collision. From
the development in Appendix C, it is straightforward to show

$$d q_R = |\vec{V}_R| \, \tau \, r^3 \sin\epsilon \sin^2\! \delta \, dr \, d\beta \, d\epsilon \, d\delta \qquad 14$$

is the volume of the five-space cylinder in question. Equation
11 is thus:

$$\frac{\partial \bar{f}_a}{\partial t} + \frac{P_{ja}}{B_{ja}} \frac{\partial \bar{f}_a}{\partial q_{ja}} + \mathcal{T}_{ja}^\bullet \frac{\partial \bar{f}_a}{\partial P_{ja}} = \iiiint (\bar{f}_a' \bar{f}_b' - \bar{f}_a \bar{f}_b) |\vec{V}_R| \, r^3 \sin\epsilon \sin^2\! \delta \, dr \, d\beta \, d\epsilon \, d\delta \, d\vec{P}_b . \qquad 15$$

Special attention must be paid to the regularity of the base
of the five-space cylinder:

$$r^3 \sin\epsilon \sin^2\! \delta \, dr \, d\beta \, d\epsilon \, d\delta \qquad 16$$

This surface may not be regular for a true rotor. In terms of
the variables of Appendix B, the surface is piecewise continuous
when

$$\cos\gamma = \sqrt{\frac{|\vec{H}|^2 + |\vec{\tau}|^2}{d^2}} \qquad 17$$

Therefore, the regularity of the collision surface is in question
until a transformation is made to from the variables of Appendix
B to the variables of Appendix C. If the collision surface is
not regular along the curve in question, the collision integral
will have to be separately evaluated over each regular surface.

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Equation 15 is identical in form to the Boltzmann equation but has an additional four independent variables corresponding to the orientation and angular momentum of the rotor. Due to this similarity, equation 15 shall be called a Boltzmann-type equation.

2. Derivation of the Conservation Equations of a Rigid Rotor

The expansion procedure of Enskog may be extended to solve the Boltzmann-type equation. We begin be developing the conservation equations for a gas composed of rigid rotor molecules.

Let $\Psi(\vec{p}_a, \vec{q}_a, t)$ be any scalar, vector, or tensor function of the molecular momentum, position, and time. The change of Ψ per unit time per unit volume at the point $\vec{q}_a$ due to collisions is

$$\int \Psi \left(\frac{\partial \bar{f}_a}{\partial t} \right)_c d\vec{p}_a = n \Delta \bar{\Psi} \qquad 18$$

where n is the number density such that

$$\int n \, d\vec{q}_a = N \qquad 19$$

By equation 15, we have:

$$\int \Psi \left(\frac{\partial \bar{f}_a}{\partial t} \right)_c d\vec{p}_a = \int \Psi \left\{ \frac{\partial \bar{f}_a}{\partial t} + \frac{p_{ia}}{B_{ia}} \frac{\partial \bar{f}_a}{\partial q_{ia}} + \bar{J}_{ia}^e \frac{\partial \bar{f}_a}{\partial p_{ia}} \right\} d\vec{p}_a \qquad 20$$

where the right-hand side of equation 20 is the change of Ψ per unit time at the point $\vec{q}_a$ due to molecular flow. By simple

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manipulations (see Appendix E), equation 20 may be transformed into Enskog's general equation of change of the property $\Psi(\vec{p}_a, \vec{q}_a, t)$:

$$\frac{\partial \overline{n\Psi}}{\partial t} + \frac{\partial}{\partial q_{ja}}\left[\overline{\frac{n p_{ja}\Psi}{B_{ja}}}\right] - n\left\{\overline{\frac{\partial \Psi}{\partial t}} + \overline{\frac{p_{ja}}{B_{ja}}\frac{\partial \Psi}{\partial q_{ja}}} + \overline{\mathcal{F}_{ja}^e \frac{\partial \Psi}{\partial p_{ja}}}\right\} \qquad 21$$

$$= n\overline{\Delta\Psi}$$

Note that the number average of the molecular properties, $\bar{B}_{ja}$, are

$$\overline{B}_{ja} = B_{ja} \quad \text{for } j=1 \to 4$$

$$\overline{B}_{5a} = I/2 \qquad\qquad 22$$

Unless noted otherwise, B_{ja} will now denote $\bar{B}_{ja}$.

For properties which are conserved during collision:

$$\overline{\Delta\Psi} = 0. \qquad\qquad 23$$

The conserved properties are the number of molecules (or mass), linear momentum, total angular momentum, and energy. Thus:

$$\Psi^1 = 1 \qquad\qquad \Rightarrow \text{conservation of number of molecules}$$

$$\Psi_i^2 = P_i \qquad \text{for } i=1,2,3 \quad \Rightarrow \text{conservation of linear momentum}$$

$$\Psi_i^3 = \alpha_i P_i \qquad \text{for } i=1\to5 \quad \Rightarrow \text{conservation of total angular momentum}$$

$$\Psi_4 = P_{ii}^2/2B_i \quad \text{for } i=1\to5 \quad \Rightarrow \text{conservation of energy}$$

where:

$$\alpha_i = \epsilon_{jik} r_j \quad \text{for } i,j,k = 1\to3$$

$$\alpha_i = \hat{e}_i \qquad \text{for } i=4,5.$$

Upon decomposing the momentum into a mean component:

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$$P_{o_j} = P_{o_j}(q_i, t) \qquad\qquad 24$$

and into a peculiar component

$$P_j \neq P_j(P_{o_j}, q_i, t) \qquad\qquad 25$$

and substituting for each conserved property into equation 22 yields the four conservation equations:

i) Continuity Equation:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n P_{o_j}}{B_j}\right] = 0 \qquad \text{for } j = 1 \to 5 \qquad 26$$

ii) Conservation of Linear Momentum:

$$n\frac{\partial P_{o_i}}{\partial t} + \frac{n P_{o_j}}{B_j}\frac{\partial P_{o_i}}{\partial q_j} + \frac{\partial}{\partial q_j}\left[\frac{n \overline{P_i P_j}}{B_j}\right] - n \mathcal{J}_i^e = 0 \qquad 27$$

$$\text{for } i = 1 \to 3 ; \; j = 1 \to 5$$

iii) Conservation of Total Angular Momentum:

$$n\frac{\partial P_{o_i}}{\partial t} + \frac{n P_{o_i}}{B_j}\frac{\partial P_{o_i}}{\partial q_j} + \frac{\partial}{\partial q_j}\left[\frac{n \overline{P_i P_j}}{B_j}\right] = 0 \qquad 28$$

$$\text{for } i = 4,5 ; \; j = 1 \to 5$$

iv) Conservation of Energy:

$$\frac{5}{2}nk\left[\frac{\partial T}{\partial t} + \frac{P_{o_j}}{B_j}\frac{\partial T}{\partial q_j}\right] + \frac{\partial}{\partial q_j}\left[\frac{n \overline{P_j P_{ii}^2}}{2 B_j B_i}\right] + \left[\frac{n \overline{P_i P_j}}{B_j}\right]\frac{\partial}{\partial q_j}\left[\frac{P_{o_i}}{B_i}\right] = 0 \qquad 29$$

$$\text{for } i,j = 1 \to 5$$

11

where the subscripts have been deleted for notational ease. Equations 26, 27, 28, and 29 are fully derived in Appendix E. Equations 27 and 28 show that conserving linear momentum and total angular momentum at a point is equivalent to separately conserving linear momentum and internal angular momentum. We may thus combine equations 27 and 28 to yield:

v) Conservation of Total Momentum at a Point:

$$n \frac{\partial \rho_{oi}}{\partial t} + \frac{n \rho_{oj}}{B_j} \frac{\partial \rho_{oi}}{\partial q_j} + \frac{\partial}{\partial q_j}\left[\frac{n \overline{P_i P_j}}{B_j}\right] - n \, \overline{J}_i^e = 0 \qquad\qquad 30$$

$$\text{for } i,j = 1 \rightarrow 5; \quad \overline{J}_4^e = \overline{J}_5^e = 0$$

The five-space stress tensor and the heat flux five vector are by definition:

$$\tau_{ij} \equiv \left[\frac{n \overline{P_i P_j}}{B_j}\right] = \int \overline{f}\left[\frac{P_i P_j}{B_j}\right] d\vec{P} \qquad\qquad 31$$

$$Q_j \equiv \left[\frac{n \overline{P_j P_{ii}^2}}{2 B_j B_i}\right] = \int \overline{f}\left[\frac{P_j P_{ii}^2}{2 B_j B_i}\right] d\vec{P} \qquad\qquad 32$$

respectively. Both τ_{ij} and Q_j are determined from the distribution function, $\overline{f}$.

3.   Enskog's Expansion Method of Solution

Under Enskog's expansion method of solution, the distribution function is assumed expandable into the convergent infinite series:

$$\overline{f} = \overline{f}^0 + \overline{f}^1 + \overline{f}^2 + \ldots \qquad\qquad 33$$

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The present analysis derives the first two terms of the series, $\bar{f}^1$ and $\bar{f}^0$.

Let the Boltzmann-type equation be defined as[1]:

$$\xi(\bar{f}) \equiv \mathcal{D}(\bar{f}) + J(\bar{f}\bar{f}_b) = 0 \qquad 34$$

where

$$\mathcal{D}(\bar{f}) \equiv \frac{\partial \bar{f}}{\partial t} + \frac{P_j}{B_j}\frac{\partial \bar{f}}{\partial q_j} + \tilde{J}_j^e \frac{\partial \bar{f}}{\partial P_j} \qquad 35$$

and

$$J(\bar{f}\bar{f}_b) \equiv -\left(\frac{\partial \bar{f}}{\partial t}\right)_c = \iint (\bar{f}\bar{f}_b - \bar{f}'\bar{f}_b')\,d_{\vec{P}_b}d_{\vec{q}_R} \; . \qquad 36$$

Enskog supposed that when the Boltzmann-type operator, ξ, operates on the above infinite series expansion of $\bar{f}$, the $r^{\underline{th}}$ term of the resulting series depends only on the first r terms, i.e.

$$\xi(\bar{f}) = \xi(\bar{f}^0 + \bar{f}^1 + \bar{f}^2 + \ldots) = \xi^0(\bar{f}^0) + \xi^1(\bar{f}^0, \bar{f}^1) + \xi^2(\bar{f}^0, \bar{f}^1, \bar{f}^2) + \ldots \qquad 37$$

The functions $\bar{f}^r$ are also assumed to satisfy the separate conditions:

$$\xi^0(\bar{f}^0) = 0$$
$$\xi^1(\bar{f}^0, \bar{f}^1) = 0 \qquad 38$$
$$\xi^2(\bar{f}^0, \bar{f}^1, \bar{f}^2) = 0 \quad \ldots$$

Enskog subdivided ξ such that

$$\xi^0 = \mathcal{D}^0 = 0 \qquad 39$$

$$\xi^r = \mathcal{D}^r + J^r = 0 \quad \text{for } r \geq 1 . \qquad 40$$

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Equation 40 may be recast[1] as:

$$J(\bar{f}^\circ \bar{f}_b^r) + J(\bar{f}^r \bar{f}_b^\circ) = -\mathcal{D}^r - J(\bar{f}^1 \bar{f}_b^{r-1}) - \ldots - J(\bar{f}^{r-1} \bar{f}_b^1).$$ 41

The general solution to equation 41 is simply the sum of the particular solution and the homogeneous solution. Let the homogeneous solution be

$$\bar{f}^r = \bar{\Phi}^r \bar{f}^\circ$$ 42

where $\bar{f}^r$ is the homogeneous solution to equation 41. Then:

$$0 = J(\bar{f}^\circ \bar{f}_b^r) + J(\bar{f}^r \bar{f}_b^\circ) = \iint \bar{f}^\circ \bar{f}_b^\circ (\bar{\Phi}^r + \bar{\Phi}_b^r - \bar{\Phi}^{r'} - \bar{\Phi}_b^{r'}) d\vec{p}_b d\vec{q}_R \equiv n^2 I(\bar{\Phi}^r)$$ 43

and therefore Φ^r must be a linear combination of the conserved properties of a collision, i.e.

$$\bar{\Phi}^r = \alpha^{1,r} + \alpha_i^{2,r} P_i + \alpha_j^{3,r} P_j + \alpha^{4,r} P_{kk}^2 / 2B_k$$ 44

where $\alpha^{1,r}$ and $\alpha^{4,r}$ are scalars, $\vec{\alpha}^{2,r}$ is a three-vector, and $\vec{\alpha}^{3,r}$ is a five-vector. The above constants are chosen such that

$$\int \bar{f}^r \psi^i d\vec{p}_a = 0 \qquad \text{for } i=1,2,3,4; \; r \geq 1$$ 45

which ensures that the average values of n, T, and $\vec{P}_0$ are given by

$$\int \bar{f}^\circ \psi^i d\vec{p}_a \qquad \text{for } i=1,2,3,4.$$ 46

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The preceeding brief overview of Enskog's method of solution brings us to the important subject of the conditions of solvability of equation 40. If equation 40 is satisfied, then

$$\int (J^r \cdot \mathcal{D}^r) \Psi^i \, d\vec{p}_a = 0 \qquad \text{for } i=1,2,3,4. \qquad 47$$

By the developments of Ref. 1, J^r is divisible into pairs of terms such as $J(\bar{f}^p \bar{f}_1^q) + J(\bar{f}^q \bar{f}_1^p)$ plus a term $J(\bar{f}^p \bar{f}_1^p)$ if p is even. It is straightforward to show that the integral of the product of Ψ^i and these terms vanishes because

$$\Psi + \Psi_b = \Psi' + \Psi'_b$$

during a collision. Thus, a necessary condition for the solution of equation 40 is:

$$\int \mathcal{D}^r \Psi^i \, d\vec{p}_a = 0 \qquad \text{for } i=1,2,3,4. \qquad 48$$

Hilbert[1] proved that the above condition is also a sufficient condition for the solution of equation 40 by showing $I(\Phi^r)$ may be expressed as

$$\Omega_o(\vec{p}) \bar{\Phi}^r(\vec{p}) + \int \Omega(\vec{p},\vec{p}_b) \bar{\Phi}^r(\vec{p}_b) \, d\vec{p}_b \qquad 49$$

where $\Omega(\vec{p},\vec{p}_b)$ is a symmetric function of $\vec{p}$, $\vec{p}_b$. Such a proof is not yet available for the present case. However, it is fully expected that

$$\iint \bar{f}^o \bar{f}_b^o (\bar{\Phi}^r + \bar{\Phi}_b^r - \bar{\Phi}^{r'} - \bar{\Phi}_b^{r'}) \, d\vec{p}_b \, d\vec{q}_R \qquad 50$$

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where $d\vec{q}_R$ is given by equation 30 is indeed expressible in the form of equation 49. By following arguments identical to those of Chapman & Cowling[1], it is straightforward to show that

$$\iint \bar{f}^\circ \bar{f}^\circ_b \bar{\Phi}^r \, d\vec{p}_b \, d\vec{q}_R = \Omega_\circ(\vec{p}) \bar{\Phi}^r(\vec{p}).$$

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It remains to show that

$$\iint \bar{f}^\circ \bar{f}^\circ_b (\bar{\Phi}'_b - \underline{\bar{\Phi}}^{r'} - \bar{\Phi}'^{r'}_b) \, d\vec{p}_b \, d\vec{q}_R = \int \Omega(\vec{p}, \vec{p}_b) \bar{\Phi}^r(\vec{p}_b) \, d\vec{p}_b$$

52

where $\Omega(\vec{p}, \vec{p}_b)$ is symmetric with respect to $\vec{p}$, $\vec{p}_b$. This is strongly felt to be true. It will be shown that $\bar{f}^0 \bar{f}^0_b$ is symmetric with respect to $\vec{p}$, $\vec{p}_b$. Since inverse collisions exist, the problem reduces to whether or not $d\vec{q}_R$ is symmetric with respect to $\vec{p}$, $\vec{p}_b$. If $d\vec{q}_R$ is not symmetric in $\vec{p}$, $\vec{p}_b$, then the principle of objectivity would be violated, i.e. the final answer would depend upon one's choice of the origin and coordinate system. Physically, this does not happen and one would therefore conclude that $d\vec{q}_R$ is indeed symmetric in $\vec{p}$, $\vec{p}_b$. A mathematical proof is required, however, to rid the present work of any ambiguities in this area. The present work shall proceed on the reasonable assumption that equation 48 is a sufficient condition for the solution of equation 40.

4. Derivation of $\bar{f}^0$

The first term $\bar{f}^0$ of the series expansion of $\bar{f}$ is easily found. By Enskog's method of division, $\mathcal{D}^0 = 0$, and the Boltzmann-type equation is:

$$O = \iiiint \left(\bar{f}^{0\prime} \bar{f}_b^{0\prime} - \bar{f}^0 \bar{f}_b^0 \right) |\vec{V}_R| \, r^3 \sin \epsilon \, \sin 2\delta \, dr \, d\beta \, d\epsilon \, d\delta \, d\vec{P}_b . \tag{53}$$

Thus, in general[1]

$$\bar{f}^{0\prime} \bar{f}_b^{0\prime} - \bar{f}^0 \bar{f}_b^0 = O \tag{54}$$

or

$$\ln \bar{f}^{0\prime} + \ln \bar{f}_b^{0\prime} = \ln \bar{f}^0 + \ln \bar{f}_b^0 \tag{55}$$

Equation 55 can hold in general only if $\ln |\bar{f}^0|$ is a linear combination of the properties conserved during collision. These properties are Ψ^i for $i = 1, 2, 3, 4$. Thus:

$$\ln \bar{f}^0 = \beta^{1,0} + \vec{\beta}^{2,0} \cdot \vec{\Psi}^2 + \vec{\beta}^{3,0} \cdot \vec{\Psi}^3 + \beta^{4,0} \Psi^4 \tag{56}$$

$$\ln \bar{f}^0 = \beta^{1,0} + \beta_j^{3,0} P_j + \beta_R^{3,0} a_i P_i + \beta^{4,0} P_{\ell\ell}^2 / 2B_\ell \tag{57}$$

$$\text{where } i, k, \ell : 1 \rightarrow 5; \quad j : 1 \rightarrow 3$$

By the development of Appendix F:

$$\bar{f}^0 = n \prod_{i=1}^{5} \left(2\pi B_i \, kT \right)^{-1/2} \exp \left(-P_i^2 / 2B_i \, kT \right) \tag{58}$$

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where B_5 is $I\sin^2\theta$, not $I/2$. The equilibrium distribution function is built on the following definitions:

$$\int \bar{f}^{\circ} d\vec{p}_a = n \tag{59}$$

$$\int \bar{f}^{\circ} \vec{p}_a \, d\vec{p}_a = n\vec{p}_o \tag{60}$$

$$\int \bar{f}^{\circ} \frac{P_{ii}^2}{2B_i} \, d\vec{p}_i = \frac{5}{2} nkT. \tag{61}$$

5. Derivation of $\bar{f}^1$

The evaluation of the second term, $\bar{f}^1$, is more difficult. By Enskog's method of division

$$\mathfrak{f}' = \mathfrak{D}' + \mathfrak{J}' = 0$$

where $\mathfrak{D}'$ operates on $\bar{f}^{\circ}$ only. Since $\bar{f}^{\circ}$ is a function only of the peculiar momentum, $\vec{P}$, we may recast $\mathfrak{D}'$ in terms of $\vec{P}$ as:

$$\mathfrak{D}' = \frac{D_o \bar{f}^{\circ}}{Dt} + \delta_{ij}\left[\bar{J}_i^e - \frac{D_o \rho_{oi}}{Dt}\right]\frac{d\bar{f}^{\circ}}{dP_i} + \frac{P_j}{B_j}\frac{d\bar{f}^{\circ}}{dq_j} - \frac{P_j}{B_j}\frac{d\bar{f}^{\circ}}{dP_i}\frac{d\rho_{oi}}{dq_j} . \tag{62}$$

The derivation of equation 62 is not presented as it is identical to the derivation presented by Chapman & Cowling[1]. The equilibrium distribution, $\bar{f}^{\circ}$, is already known and the first approximations

$$\frac{D_o \rho_{oi}}{Dt} , \quad \frac{D_o T}{Dt}$$

may be found from the conservation equations and Enskog's subdivision of $\mathfrak{D}$. The conservation equations, equations 26, 30, and 29, may be recast as:

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$$\frac{\partial n}{\partial t} = -\frac{\partial}{\partial q_j}\left[\frac{n p_{oj}}{B_j}\right] \qquad 63$$

$$\frac{\partial p_{oi}}{\partial t} = \mathcal{F}_i^e - \frac{p_{oj}}{B_j}\frac{\partial p_{oi}}{\partial q_j} - \frac{1}{n}\frac{\partial}{\partial q_j}\left[\frac{n\overline{P_i P_j}}{B_j}\right] \qquad 64$$

$$\frac{\partial T}{\partial t} = \frac{-p_{oj}}{B_j}\frac{\partial T}{\partial q_j} - \frac{2}{snk}\left\{\frac{\partial}{\partial q_j}\left[\frac{n\overline{P_j P_{ii}^2}}{2B_j B_i}\right] + \left[\frac{n\overline{P_i P_j}}{B_j}\right]\frac{\partial}{\partial q_j}\left[\frac{p_{oi}}{B_i}\right]\right\} \qquad 65$$

respectively. Enskog divided these time derivatives as follows:

$$\frac{\partial \Lambda}{\partial t} = \sum_{r=0}^{\infty}\frac{\partial_r \Lambda}{\partial t} \qquad 66$$

where Λ may be either n, $\vec{p}_0$, or T. The division of the right-hand side is:

$$\frac{\partial_o n}{\partial t} = -\frac{\partial}{\partial q_j}\left[\frac{n p_{oj}}{B_j}\right] \qquad 67$$

$$\frac{\partial_r n}{\partial t} = 0 \qquad \text{for } r \geq 1 \qquad 68$$

$$\frac{\partial_o p_{oi}}{\partial t} = \mathcal{F}_i^e - \frac{p_{oj}}{B_j}\frac{\partial p_{oi}}{\partial q_j} - \frac{1}{n}\frac{\partial}{\partial q_j}\tau_{ij}^o \qquad 69$$

$$\frac{\partial_r p_{oi}}{\partial t} = -\frac{1}{n}\frac{\partial}{\partial q_j}\tau_{ij}^r \qquad \text{for } r \geq 1 \qquad 70$$

$$\frac{\partial_o T}{\partial t} = \frac{-p_{oj}}{B_j}\frac{\partial T}{\partial q_j} - \frac{2}{snk}\left\{\frac{\partial}{\partial q_j}q_j^o + \tau_{ij}^o\frac{\partial}{\partial q_j}\left[\frac{p_{oi}}{B_i}\right]\right\} \qquad 71$$

$$\frac{\partial_r T}{\partial t} = \frac{-2}{snk}\left\{\frac{\partial}{\partial q_j}q_j^r + \tau_{ij}^r\frac{\partial}{\partial q_j}\left[\frac{p_{oi}}{B_i}\right]\right\} \qquad \text{for } r \geq 1 \qquad 72$$

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where

$$\tau_{ij} = \sum_{r=0}^{\infty} \tau_{ij}^{r} \quad ; \quad Q_{j} = \sum_{r=0}^{\infty} Q_{j}^{r} \qquad\qquad 73$$

and

$$\tau_{ij}^{r} = \int \bar{f}^{r} \left[\frac{P_{i} P_{j}}{B_{j}} \right] d\vec{P} \qquad\qquad 74$$

$$Q_{j}^{r} = \int \bar{f}^{r} \left[\frac{P_{j} P_{ii}^{2}}{2 B_{j} B_{i}} \right] d\vec{P}. \qquad\qquad 75$$

By defining the first approximation to the substantive derivative as:

$$\frac{D_{o}}{Dt} \equiv \frac{\partial}{\partial t} + \frac{P_{oj}}{B_{j}} \frac{\partial}{\partial q_{j}}$$

equations 62 and 63 become:

$$\frac{D_{o} P_{oi}}{Dt} = \mathcal{J}_{i}^{e} - \frac{1}{n} \frac{\partial}{\partial q_{j}} \tau_{ij}^{o} \qquad\qquad 76$$

$$\frac{D_{o} T}{Dt} = \frac{-2}{5nk} \left\{ \frac{\partial}{\partial q_{j}} Q_{j}^{o} + \tau_{ij}^{o} \frac{\partial}{\partial q_{j}} \left[\frac{P_{oi}}{B_{i}} \right] \right\}. \qquad\qquad 77$$

When r is zero, only the even terms of the integrands of equations 74 and 75 survive the integration. Thus,

$$Q_{j}^{o} = 0 \qquad\qquad 78$$

and by the definitions and results of Appendix F:

$$\tau_{ij}^{o} = nkT \delta_{ij} \qquad\qquad 79$$

By defining the thermodynamic pressure as

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$$p = nkT \tag{80}$$

then

$$\tau_{ij}^{\circ} = p\delta_{ij} \ . \tag{81}$$

The thermodynamic pressure may not equal the hydrostatic pressure. However, the hydrostatic pressure cannot be deduced because Maxwell's relations are strictly valid for a three-dimensional space only. Thus, Maxwell's relation:

$$p = -(\frac{\partial A}{\partial V})_T = kT(\frac{\partial \ln Z}{\partial V})_T$$

cannot be used in the present study.

Substituting the first approximations to the heat flux vector and the stress tensor into equations 76 and 77 yields:

$$\frac{D_o p_{oi}}{Dt} = \mathcal{F}_i^e - \frac{1}{n}\delta_{ij}\frac{\partial p}{\partial q_j} \tag{82}$$

$$\frac{D_o T}{Dt} = \frac{-2T}{5}\frac{\partial}{\partial q_i}\left[\frac{p_{oi}}{\beta_i}\right] \ . \tag{83}$$

Substituting equation 82 into equation 62 yields:

$$\mathcal{D}' = \bar{f}^{\circ}\left\{\frac{D_o \ln \bar{f}^{\circ}}{Dt} + \frac{\delta_{ij}}{n}\frac{\partial p}{\partial q_j}\frac{\partial \ln \bar{f}^{\circ}}{\partial P_i} + \frac{P_j}{\beta_j}\frac{\partial \ln \bar{f}^{\circ}}{\partial q_j} - \frac{P_j}{\beta_j}\frac{\partial \ln \bar{f}^{\circ}}{\partial P_i}\frac{\partial p_{oi}}{\partial q_j}\right\} \ . \tag{84}$$

Appendix H reduces equation 84 and finds that $\xi^1 = 0$ is equivalent to:

$$n^2 I(\underline{\Sigma}') = -\bar{f}^{\circ}\left\{\left(\frac{2kT}{\beta_j}\right)^{1/2}\left(\mathcal{P}_{ii}^2 - \frac{3}{2}\right)\mathcal{P}_j + 2\left(\frac{\beta_j}{\beta_i}\right)^{1/2}\frac{\mathcal{P}_i^{\circ}\mathcal{P}_j}{\beta_j}\frac{\partial p_{oi}}{\partial q_j}\right\} \tag{85}$$

where $\mathcal{P}_i$, the reduced momentum, is defined as:

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$$\wp_i = \frac{P_i}{(2B_i kT)^{1/2}}$$

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Appendix H derives the form of Φ^1 as:

$$\bar{\Phi}' = \frac{-1}{n}\left[\left(\frac{2kT}{B_j}\right)^{1/2} J(\wp)\wp_j \frac{\partial \ln T}{\partial q_j} + \left(\frac{B_i}{B_i}\right)^{1/2} k(\wp)\left[\frac{\wp_i^\circ \wp_j}{B_j}\right] \frac{\partial P_{o i}}{\partial q_j}\right]$$

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where $J(\wp)$ and $K(\wp)$ are scalar functions of $\vec{P}$, n, and T.
    Substituting

$$\bar{f}' = \bar{\Phi}'\bar{f}^\circ$$

for $\bar{f}$ in the definitions of the five-space stress tensor and the
heat flux five vector determines the second order approximations
of τ_{ij} and Q_j.   Appendix I details the derivations of τ_{ij}^1 and Q_j^1.
The resulting expressions are:

$$\tau_{ij}' = \frac{-kT}{14}\left(\frac{B_i}{B_j}\right)^{1/2} \frac{\partial P_{o i}^{as}}{\partial q_j} \int_{-\infty}^{+\infty} k_{ij} \bar{I}(k_{ij}) d\vec{p}$$

88

$$= -2\mu\left(\frac{B_i}{B_j}\right)^{1/2} \frac{\partial P_{o i}^{as}}{\partial q_j}$$

89

where

$$\mu \equiv \frac{kT}{28} \int k_{ij} \bar{I}(k_{ij}) d\vec{p}$$

90

and

$$Q_j' = \frac{-2k^2 T}{5n B_j} \frac{\partial T}{\partial q_j} \int \bar{f}^\circ \wp^4 J(\wp) d\vec{p}$$

91

$$= \frac{-\lambda}{B_j} \frac{\partial T}{\partial q_j}$$

92

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where

$$\lambda = \frac{2k^2 T}{5n} \int \bar{f} \cdot (P^4 J(P) \, d\vec{P}.$$
93

    Appendix J evaluates μ and λ through the use of Sonine polynomials. Assuming that the first term of the Sonine polynomial is of sufficient accuracy, Appendix J shows:

$$\mu = \frac{7kT}{b_{11}}$$
94

$$\lambda = \frac{245}{8} \frac{k^2 T}{a_{11}}$$
95

$$P_r = .8 \frac{a_{11}}{b_{11}}$$
96

where the terms a_{11} and b_{11} can be evaluated only when the intermolecular potential is known. Since the intermolecular potential of the present problem is simply a pair of Heaviside step functions, a_{11} and b_{11} could be evaluated. Such an evaluation is likely to be very difficult. Given the assumption of impulsive collisions, the evaluation is also prone to be in significant error with respect to the experimentally measured values. Therefore, neither a_{11} nor b_{11} have been evaluated.

SUMMARY OF DERIVED EQUATIONS, CONSTANTS, AND ASSUMPTIONS

The equations of motion of a diatomic gas whose molecules may be modelled as rigid rotors are:

1) Conservation of the Number of Molecules:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n P_{oi}}{B_j}\right] = 0 \qquad \text{for } j = 1 \to 5$$

2) Conservation of Total Momentum at a Point:

$$n\frac{\partial P_{oi}}{\partial t} + \frac{n P_{oj}}{B_j}\frac{\partial P_{oi}}{\partial q_j} + \frac{\partial}{\partial q_j}\left[\tau_{ij}\right] - n \mathcal{J}_i^e = 0 \qquad \text{for } i,j = 1 \to 5$$

where:

$$\vec{\mathcal{J}}_4^e = \vec{\mathcal{J}}_5^e = 0$$

$$\tau_{ij} = p\,\delta_{ij} - 2\mu\left(\frac{B_i}{B_j}\right)^{1/2}\frac{\partial P_{oi}}{\partial q_j}$$

$$\mu = 7kT/b_{11}$$

3) Conservation of Energy:

$$\frac{5}{2}nk\left[\frac{\partial T}{\partial t} + \frac{P_{oj}}{B_j}\frac{\partial T}{\partial q_j}\right] + \frac{\partial Q_j}{\partial q_j} + \tau_{ij}\frac{\partial}{\partial q_j}\left[\frac{P_{oi}}{B_i}\right] = 0 \qquad \text{for } i,j = 1 \to 5$$

where

$$Q_j = \frac{-\lambda}{B_j}\frac{\partial T}{\partial q_j}$$

$$\lambda = \frac{245}{8}\frac{k^2 T}{a_{11}}$$

4) Equation of State:

$$p = nkT$$

where p is, by definition, the thermodynamic pressure.

Additional quantities of interest are:

i) Specific Heats:

$$C_v = 2.5\, nk \; ; \; C_p = 3.5\, nk$$

ii) Ratio of Specific Heats:

$$\gamma = 1.400$$

iii) Prandtl Number:

$$P_r = .8 \frac{a_{11}}{b_{11}}$$

iv) Equilibrium Distribution Function:

$$\bar{f}^\circ = n \prod_{i=1}^{5} \left(2\pi B_i kT\right)^{-1/2} \exp\left(-P_i^2 / 2 B_i kT\right)$$

Most assumptions made in the present analysis are identical to those of the derivation of the conventional Navier-Stokes equations. Those assumptions unique to the present analysis are listed below:

1) The molecules nonpolar. This amounts to setting $F_4^e = F_5^e = 0$.

2) The intermolecular collisions are impulsive.

3) That

$$\int \Psi^i \mathcal{D}^r d\vec{P_\alpha} = 0$$

is a sufficient condition for the Enskog expansion method of solution of equation 15. This appears to be a reasonable

assumption based on physical arguments, the form of $\bar{f}^0$, and the existence of inverse collisions. Strictly speaking, however, the sufficiency condition is an assumption and a rigorous proof is needed.

SECTION IV

DISCUSSION

We have seen that a nonpolar diatomic gas whose molecules collide impulsively obeys a Boltzmann-type equation, namely equation 15. The differential portion of the equation is easily developed by substituting the well known Hamiltonian of a rigid rotor into the Liouville equation. The collision integral is developed along the lines of Kirkwood's work[8,9] Appendix B develops the actual governing equations of motion of a binary collision between rigid rotors. Appendix B displays the fundamental point that inverse collisions exist as long as the collision mechanics are consistent with the Hamiltonian. The rough sphere molecular model[6] suffers in this regard, as the Hamiltonian does not account for the strain energy of the rough sphere during collision.

The derivation of the differential portion of the Boltzmann-type equation is not the straightforward extension from three degrees of freedom assumed by others[6,7,8] In fact, an additional term describing the precession of the rotor is generally present. Only when the molecules are nonpolar and collide impulsively does this precessional term vanish. Furthermore, it is unlikely that a general Boltzmann-type equation can be derived for a rigid, six degree of freedom molecule. Consider the classical Hamiltonian for such a molecule[3]:

$$H = \frac{1}{2m}\{p_x^2 + p_y^2 + p_z^2\} + \frac{1}{2I_A \sin^2\theta}\left[(p_\phi - p_\psi \cos\theta)\cos\psi - p_\theta \sin\theta \sin\psi\right]^2$$

$$+ \frac{1}{2I_B \sin^2\theta}\left[(p_\phi - p_\psi \cos\theta)\sin\psi + p_\theta \sin\theta \cos\psi\right]^2 + \frac{1}{2I_C}p_\psi^2$$

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where I_A, I_B, and I_C are the principal moments of inertia; θ, ϕ, and ψ are the Euler angles, and

$$0 \leq \theta \leq \pi$$
$$0 \leq \phi \leq 2\pi$$
$$0 \leq \psi \leq 2\pi.$$

Substituting the above Hamiltonian into the Liouville equation produces a complicated equation in f. There are many terms describing the precession of a general rotation to a rotation about an axis of minimum or maximum moment of inertia. These precessional terms do not disappear when the molecule is assumed to be nonpolar and to collide impulsively. The rigid rotor molecule thus appears to be the most complex molecule that obeys a Boltzmann-type equation with a minimum of assumptions. Molecular models of six degrees of freedom and more, such as the non-rigid rotor, the symmetric top, and the asymmetric top, may require an approach based upon a pair or triple distribution function.

The assumptions of the present study mirror those in the development of the Navier-Stokes equations, except in four instances. One of the assumptions different from those of the Navier-Stokes equations is the basis of the present study, namely that the gas molecule can be modelled as a rigid rotor. The two additional assumptions of impulsive collisions and nonpolar molecules eliminate the precessional term from the Boltzmann-type equation. The fourth assumption that

$$\int \Upsilon^i \mathcal{D}^r d\vec{p_\alpha} = 0$$

is a sufficient condition for the solution of

$$\mathcal{D}^r + J^r = 0$$

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is critical to the development of the stress tensor and the heat flux vector. If that assumption is false, then $I(\Phi^r)$ is asymmetric with respect to $\vec{p}_a$ and $\vec{p}_b$. The collisional equations of motion would then change upon an interchange of the roles of molecules a and b. The physics of the motion, however, does not depend upon how we select molecules a and b. Therefore, this sufficiency assumption is probably correct. A rigorous proof similar to Hilbert's[1] treatment in three degrees of freedom is required, however, to close the discussion on this issue.

The stress tensor is expanded in Fig. 1. Those terms containing angular quantities, θ, ϕ, $I\dot{\theta}$, and $I\dot{\phi}$, are periodic because the Euler angles are periodic. Also, there are seven coefficients of "viscosity". These coefficients of viscosity and their orders of magnitude relative to the usual shear viscosity, μ, are displayed in Table 2.

Table 2. Relative Magnitudes of the Viscosity Coefficients

Coefficient of Viscosity	Relative Order of Magnitude
μ	1
$\sqrt{2}\,\mu$	1
$\mu/\sqrt{2}$	1
μr_g	$10^{-10}\,m$
$\mu r_g/\sqrt{2}$	$10^{-10}\,m$
μ/r_g	$10^{10}\,m^{-1}$
$\sqrt{2}\,\mu/r_g$	$10^{10}\,m^{-1}$

$$\tau_{ij} = \begin{bmatrix}
p-2\mu\left[\dfrac{\partial mu}{\partial x}-\Delta\right] & -\mu\left[\dfrac{\partial mv}{\partial x}+\dfrac{\partial mu}{\partial y}\right] & -\mu\left[\dfrac{\partial mw}{\partial x}+\dfrac{\partial mu}{\partial z}\right] & \dfrac{-\mu}{r_g}\left[\dfrac{\partial I\dot\theta}{\partial x}+\dfrac{\partial mu}{\partial \theta}\right] & \dfrac{-\sqrt2\mu}{r_g}\left[\dfrac{\partial I\dot\theta}{2\partial x}+\dfrac{\partial mu}{\partial \phi}\right] \\[2.2em]
-\mu\left[\dfrac{\partial mu}{\partial y}+\dfrac{\partial mv}{\partial x}\right] & p-2\mu\left[\dfrac{\partial mv}{\partial y}-\Delta\right] & -\mu\left[\dfrac{\partial mw}{\partial y}+\dfrac{\partial mv}{\partial z}\right] & \dfrac{-\mu}{r_g}\left[\dfrac{\partial I\dot\theta}{\partial y}+\dfrac{\partial mv}{\partial \theta}\right] & \dfrac{-\sqrt2\mu}{r_g}\left[\dfrac{\partial I\dot\theta}{2\partial y}+\dfrac{\partial mv}{\partial \phi}\right] \\[2.2em]
-\mu\left[\dfrac{\partial mu}{\partial z}+\dfrac{\partial mw}{\partial x}\right] & -\mu\left[\dfrac{\partial mv}{\partial z}+\dfrac{\partial mw}{\partial y}\right] & p-2\mu\left[\dfrac{\partial mw}{\partial z}-\Delta\right] & \dfrac{-\mu}{r_g}\left[\dfrac{\partial I\dot\theta}{\partial z}+\dfrac{\partial mw}{\partial \theta}\right] & \dfrac{-\sqrt2\mu}{r_g}\left[\dfrac{\partial I\dot\theta}{2\partial z}+\dfrac{\partial mw}{\partial \phi}\right] \\[2.2em]
-\mu r_g\left[\dfrac{\partial mu}{\partial \theta}+\dfrac{\partial I\dot\theta}{\partial x}\right] & -\mu r_g\left[\dfrac{\partial mv}{\partial \theta}+\dfrac{\partial I\dot\theta}{\partial y}\right] & -\mu r_g\left[\dfrac{\partial mw}{\partial \theta}+\dfrac{\partial I\dot\theta}{\partial z}\right] & p-2\mu\left[\dfrac{\partial I\dot\theta}{\partial \theta}-\Delta\right] & \dfrac{-\mu}{\sqrt2}\left[\dfrac{\partial I\dot\theta}{\partial \phi}+\dfrac{\partial I\dot\theta}{2\partial \theta}\right] \\[2.2em]
\dfrac{-\mu r_g}{\sqrt2}\left[\dfrac{\partial mu}{\partial \phi}+\dfrac{\partial I\dot\theta}{2\partial x}\right] & \dfrac{-\mu r_g}{\sqrt2}\left[\dfrac{\partial mv}{\partial \phi}+\dfrac{\partial I\dot\theta}{2\partial y}\right] & \dfrac{-\mu r_g}{\sqrt2}\left[\dfrac{\partial mw}{\partial \phi}+\dfrac{\partial I\dot\theta}{2\partial z}\right] & -\sqrt2\mu\left[\dfrac{\partial I\dot\theta}{2\partial \theta}+\dfrac{\partial I\dot\theta}{\partial \phi}\right] & p-2\mu\left[\dfrac{\partial I\dot\theta}{2\partial \phi}-\Delta\right]
\end{bmatrix}$$

where:

$$\Delta \equiv \frac{1}{5}\left[\frac{\partial mu}{\partial x}+\frac{\partial mv}{\partial y}+\frac{\partial mw}{\partial z}+\frac{\partial I\dot\theta}{\partial \theta}+\frac{\partial I\dot\theta}{2\partial \phi}\right]$$

Figure 1. Stress Tensor

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The molecular radius of gyration is r_g. The relative orders of magnitude of the seven coefficients of viscosity are based upon a typical value of r_g of 10^{-10} meters. The first three columns of the stress tensor generate changes in linear momentum. We see the periodic terms probably contribute negligible changes in linear momentum because of their very small coefficient of viscosity. The periodic terms will perhaps be significant only in shock layers where the gradients are large.

One should also note that a gas composed of rigid rotor molecules may have a bulk viscosity. The bulk viscosity will be due to the rotational degrees of freedom responding to energy gradients at a rate different from the response rate of the translational degrees of freedom.

The derivation of the Prandtl number is unfinished. The ratio of a_{11}/b_{11} is unity for the rigid, smooth-sphere molecular model. If this is found to hold for rigid rotors, the Prandtl number will be .8 -- a mediocre prediction. See Table 1.

The present work forms the foundation upon which a study into the properties of a gas composed of non-rigid rotors can be built. It would be most interesting to establish the Liouville equation in terms of a pair-distribution function and then substitute for the Hamiltonian of each atom of the rotor. The Hamiltonian must include the quantized intermolecular potential that holds together the rotor. If this approach is possible not only vibration, but disassociation, could be included into the governing equations of motion. The resulting equations should model the important real gas effects of hypersonic flows.

SECTION V

CONCLUSION

One may develop the equations of motion of a diatomic gas by substituting the Hamiltonian of a rigid rotor into the Liouville equation. The equations mirror the Navier-Stokes equations except with regard to an additional two equations conserving angular momentum, the stress tensor, and certain molecular constants. The assumptions of the present derivation are identical to those in the development of the Navier-Stokes equations except that the molecules are nonpolar and collide impulsively. Intriguing because it resides in a five-dimensional space, the development is a stepping-stone to a study which will include the vibration and disassociation of a diatomic gas.

APPENDIX A
Kirkwood's Development of the Collision Integral

By Gibbs' postulate, the ensemble average of any molecular function, $\Psi(\vec{p}_N, \vec{q}_N)$ is the macroscopically observed value:

$$\Psi_{obs} = \iint \Psi(\vec{p}_N, \vec{q}_N) \, {}^{\gamma}f^{(N)}(\vec{p}_N, \vec{q}_N, t) \, d\vec{p}_N \, d\vec{q}_N \qquad \text{A.1}$$

Kirkwood[8] argues further that the measurement of any macroscopic property is an inherent time averaging operation. Therefore,

$$\Psi_{meas} = \frac{1}{\tau} \int_0^{\tau} \iint \Psi(\vec{p}_N, \vec{q}_N) \, {}^{\gamma}f^{(N)}(\vec{p}_N, \vec{q}_N, t+s) \, d\vec{p}_N \, d\vec{q}_N \, ds \qquad \text{A.2}$$

where the time interval, τ, is long in comparison to collision durations but short in comparison to a Poincaré cycle[8]. Kirkwood also shows that the measured value of any molecular function, $\Psi(\vec{p}_a, \vec{q}_a)$ is

$$\Psi_{meas} = \iint \Psi(\vec{p}_a, \vec{q}_a) \, \overline{{}^{\gamma}f_a^{(N)}}(\vec{p}_a, \vec{q}_a, t) \, d\vec{p}_a \, d\vec{q}_a \qquad \text{A.3}$$

where

$$\overline{{}^{\gamma}f_a^{(N)}}(\vec{p}_a, \vec{q}_a, t) = \frac{1}{\tau} \int_0^{\tau} {}^{\gamma}f_a^{(N)}(\vec{p}_a, \vec{q}_a, t+s) \, ds \qquad \text{A.4}$$

Recasting equation 11 of the text in terms of the time-averaged distribution function leads to:

$$\frac{\partial \overline{{}^{\gamma}f_a^{(N)}}}{\partial t} + \frac{P_{ja}}{B_{ja}} \frac{\partial \overline{{}^{\gamma}f_a^{(N)}}}{\partial q_{ja}} + \mathcal{I}_{ja}^e \frac{\partial \overline{{}^{\gamma}f_a^{(N)}}}{\partial p_{ja}} = -\frac{\partial}{\partial p_{ja}} \left\{ \frac{1}{\tau} \int_0^{\tau} \iint \mathcal{I}_{ja}^i \, {}^{\gamma}f^{(N)}(\vec{p}_N, \vec{q}_N, t+s) \, d\vec{p}_N \, d\vec{q}_N \, ds \right\} \qquad \text{A.5}$$

Through the use of the Dirac delta function, the collision integral may be extended over all γ-space:

$$\int_o^\tau \iint \bar{\mathfrak{J}}_{ja}^i(t)\, {}^\gamma f^{(N)}(\vec{p}_N,\vec{q}_N,t+s)\, d\vec{p}_n\, d\vec{q}_n\, ds = \int_o^\tau \iiiint \bar{\mathfrak{J}}_{ja}^i(t)\, {}^\gamma f^{(N)}(\vec{p}_N,\vec{q}_N,t+s)\, \delta(\vec{p}_{a_o}+\Delta\vec{p}_a-\vec{p}_a)\, \cdot \qquad \text{A.6}$$

$$\cdot\, \delta(\vec{q}_{a_o}+\Delta\vec{q}_a-\vec{q}_a)\, d\vec{p}_n\, d\vec{q}_n\, d\vec{p}_a\, d\vec{q}_a\, ds$$

where

$$\Delta P_{ja} = \int_o^s \bar{\mathfrak{J}}_{ja}^i(t+s')\, ds' + \bar{\mathfrak{J}}_{ja}^e s$$

$$\Delta q_{ja} = \int_o^s \frac{P_{ja}}{B_{ja}}\, ds'$$

The subscript o denotes a value at some initial instant of time, t. By the principle of conservation of extension in phase space:

$$\int_o^\tau \iint \bar{\mathfrak{J}}_a^i(t)\, {}^\gamma f^{(N)}(\vec{p}_N,\vec{q}_N,t+s)\, d\vec{p}_n\, d\vec{q}_n\, ds = \int_o^\tau \iint \bar{\mathfrak{J}}_a^i(t+s)\, {}^\gamma f^{(N)}(\vec{p}_{N_o},\vec{q}_{N_o},t)\, \delta(\vec{p}_{a_o}+\Delta\vec{p}_a-\vec{p}_a)\, \cdot \qquad \text{A.7}$$

$$\cdot\, \delta(\vec{q}_{a_o}+\Delta\vec{q}_a-\vec{q}_a)\, d\vec{p}_{n_o}\, d\vec{q}_{n_o}\, d\vec{p}_{a_o}\, d\vec{q}_{a_o}\, ds\, .$$

The gas shall be considered sufficiently dilute so that binary collisions are the sole mechanism of the collisional transfer of molecular properties. Since the collisions are impulsive, the intermolecular potential is a set of Heaviside step functions. The potential due to any molecule a is zero outside a certain volume of influence, V. Therefore, in the region of configuration space exclusive of

$$\sum_{\ell=1}^N V^\ell$$

the gas is in "molecular chaos". Kirkwood shows that for a dilute gas in molecular chaos:

$$^\gamma f^{(N)}(\vec{p}_N,\vec{q}_N,t) = {}^\gamma f_a^{(1)}(\vec{p}_a,\vec{q}_a,t)\, {}^\gamma f_b^{(1)}(\vec{p}_b,\vec{q}_b,t)\, . \qquad \text{A.8}$$

By way of equation two of the text, this leads to:

$$\frac{\partial \overline{\tau_a^{(1)}}}{\partial t} + \frac{P_{ja}}{B_{ja}} \frac{\partial \overline{\tau_a^{(1)}}}{\partial q_{ja}} + \mathcal{J}_{jc}^{e} \frac{\partial \overline{\tau_c^{(1)}}}{\partial p_{ja}} = -\frac{\partial}{\partial p_{ja}} \left\{ \frac{1}{\tau} \int_0^\tau \iiiint \mathcal{J}_{ic}^{i}(t+s) \, {}^r\mathfrak{f}_a^{(1)}(\vec{p}_{a_0},\vec{q}_{a_0},t) \, {}^r\mathfrak{f}_b^{(1)}(\vec{p}_{b_0},\vec{q}_{b_0},t) \cdot \right.$$

$$\left. \cdot \delta(\vec{p}_{a_0}+\Delta\vec{p}_a-\vec{p}_c)\,\delta(\vec{q}_{a_0}+\Delta\vec{q}_a-\vec{q}_a)\,d\vec{p}_{b_0}\,d\vec{q}_{b_0}\,d\vec{p}_{a_0}\,d\vec{q}_{a_0}\,ds \right\}. \qquad \text{A.9}$$

Since the intermolecular collisions are impulsive, the time
interval τ may be made arbitrarily short. Thus:

$$\lim_{\tau \to 0} \left\{ \delta(\vec{q}_{b_0}+\Delta\vec{q}_a-\vec{q}_a) \right\} = \delta(\vec{q}_{a_0}-\vec{q}_a) \qquad \text{A.10}$$

Assuming the above to be true for

$$\tau = 0^+$$

equation A.9 may be integrated at once:

$$\frac{\partial \overline{\tau_a^{(1)}}}{\partial t} + \frac{P_{ja}}{B_{ja}} \frac{\partial \overline{\tau_a^{(1)}}}{\partial q_{ja}} + \tilde{\mathcal{J}}_{ja}^{e} \frac{\partial \overline{\tau_a^{(1)}}}{\partial p_{ja}} = \frac{\partial}{\partial p_{ja}} \left\{ \frac{1}{\tau} \int_0^\tau \iiint \tilde{\mathcal{J}}_a^{i}(t+s) \, {}^r\mathfrak{f}_a^{(1)}(\vec{p}_{a_0},\vec{q}_{a_0},t) \, {}^r\mathfrak{f}_b^{(1)}(\vec{p}_{b_0},\vec{q}_{b_0},t) \cdot \right.$$

$$\left. \cdot \delta(\vec{p}_{a_0}+\Delta\vec{p}_a-\vec{p}_a)\,d\vec{p}_{b_0}\,d\vec{q}_{b_0}\,d\vec{p}_{a_0}\,ds \right\}. \qquad \text{A.11}$$

By Newton's second law of motion, Kirkwood recast the collision
integral as:

$$\iiint \left\{ \frac{1}{\tau} \int_0^\tau \frac{\partial}{\partial(\Delta p_{ja})} \left(\frac{\partial(\Delta p_{ja})}{\partial s} \right) \delta(\vec{p}_{a_0}+\Delta\vec{p}_a-\vec{p}_a)\,ds \right\} \, {}^r\mathfrak{f}_a^{(1)}(\vec{p}_{a_0},\vec{q}_{a_0},t) \, {}^r\mathfrak{f}_b^{(1)}(\vec{p}_{b_0},\vec{q}_{b_0},t)\,d\vec{p}_{b_0}\,d\vec{q}_{b_0}\,d\vec{p}_{a_0} \qquad \text{A.12}$$

$$\iiint \frac{1}{\tau} \left\{ \delta(\vec{p}_{a_0}+\Delta\vec{p}_a(\tau)-\vec{p}_a) - \delta(\vec{p}_{a_0}-\vec{p}_a) \right\} \, {}^t\mathfrak{f}_a^{(1)}(\vec{p}_{a_0},\vec{q}_{a_0},t) \, {}^t\mathfrak{f}_b^{(1)}(\vec{p}_{b_0},\vec{q}_{b_0},t)\,d\vec{p}_{b_0}\,d\vec{q}_{b_0}\,d\vec{p}_{a_0} \qquad \text{A.13}$$

The gas shall be considered to be composed of identical
indistinguishable molecules. Equations A.12 and A.13 may be
recast to apply to molecule phase space, μ-space. Noting:

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$$^{\mu}f^{(\mu)}(\vec{p}_a, \vec{q}_a, t) = \frac{N!}{(N-\mu)!} \, ^{\nu}f^{(\mu)}(\vec{p}_a, \vec{q}_a, t) \qquad \text{A.14}$$

and

$$^{\mu}f_a^{(1)}(\vec{p}_a, \vec{q}_a, t) = N \, ^{\nu}f_a^{(1)}(\vec{p}_a, \vec{q}_a, t) \qquad \text{A.15}$$

leads to:

$$\frac{\partial \overline{^{\mu}f_a^{(1)}}}{\partial t} + \frac{p_{ic}}{B_{ic}} \frac{\partial \overline{^{\mu}f_a^{(1)}}}{\partial q_{ia}} \cdot \mathcal{J}_{ic}^e \frac{\partial \overline{^{\mu}f_a^{(1)}}}{\partial p_{ic}} \cdot \frac{1}{\tau} \iiint \left\{ \delta(\vec{p}_{c_0} + \Delta \vec{p}_a(\tau) - \vec{p}_c) - \delta(\vec{p}_a - \vec{p}_c) \right\} \, ^{\mu}f_a^{(1)}(\vec{p}_{c_0}, \vec{q}_{a_0}, t) \, ^{\mu}f_b^{(1)}(\vec{p}_{b_0}, \vec{q}_{b_0}, t) \cdot \qquad \text{A.16}$$

$$\cdot \, d\vec{p}_{b_0} \, d\vec{q}_{b_0} \, d\vec{p}_{a_0}$$

$$\iint {}^{\mu}f_a^{(1)}(\vec{p}_a, \vec{q}_a, t) \, d\vec{p}_a \, d\vec{q}_a = N \qquad \text{A.17}$$

$$\iint \psi(\vec{p}_a, \vec{q}_a) \, ^{\mu}f_a^{(1)}(\vec{p}_a, \vec{q}_a, t) \, d\vec{p}_a \, d\vec{q}_a = N \psi_{meas} = N \overline{\psi} \qquad \text{A.18}$$

Without any loss of generality, $\vec{q}_{bo}$ may be expressed relative to

$\vec{q}_{ao}$. Denoting this relative spatial coordinate $\vec{q}_{Ro}$ and dropping

the superscripts from the μ-space probability density leads to:

$$\frac{\partial \overline{f_a}}{\partial t} + \frac{p_{ic}}{B_{ic}} \frac{\partial \overline{f_a}}{\partial q_{ia}} + \mathcal{J}_{ic}^e \frac{\partial \overline{f_a}}{\partial p_{ic}} = \frac{1}{\tau} \iiint \left\{ \delta(\vec{p}_{c_0} + \Delta \vec{p}_a(\tau) - \vec{p}_c) - \delta(\vec{p}_a - \vec{p}_c) \right\} f_a(\vec{p}_{a_0}, \vec{q}_{a_0}, t) \, f_b(\vec{p}_{b_0}, \vec{q}_{b_0}, t) \cdot \qquad \text{A.19}$$

$$\cdot \, d\vec{p}_{b_0} \, d\vec{q}_{R_0} \, d\vec{p}_{a_0}$$

This may be integrated at once:

$$\frac{\partial \overline{f_a}}{\partial t} + \frac{p_{ia}}{B_{ia}} \frac{\partial \overline{f_a}}{\partial q_{ia}} + \mathcal{J}_{ia}^e \frac{\partial \overline{f_a}}{\partial p_{ia}} = \frac{1}{\tau} \iint \left\{ f_a(\vec{p}_a - \Delta \vec{p}(\tau), \vec{q}_a, t) \, f_b(\vec{p}_b + \Delta \vec{p}(\tau), \vec{q}_b, t) - f_a(\vec{p}_a, \vec{q}_a, t) \cdot \qquad \text{A.20}$$

$$\cdot \, f_b(\vec{p}_b, \vec{q}_b, t) \right\} \, d\vec{p}_b \, d\vec{q}_R$$

since, by Newton's third law of motion:

$$\Delta \vec{p}_{a_b} = -\Delta \vec{p}_{b_a} \equiv \Delta \vec{p}$$

By invoking the principle of conservation of extension in phase space and by performing a second time-averaging operation over τ gives

$$\frac{\partial \bar{f}_a}{\partial t} + \frac{p_{ia}}{B_{ia}} \frac{\partial \bar{f}_a}{\partial q_{ic}} + \bar{J}_{ic}^e \frac{\partial \bar{f}_a}{\partial p_{ia}} = \frac{1}{\tau} \iint \overline{\{ f_a(\vec{p}_a - \Delta \vec{p}(\tau), \vec{q}_a, t) f_b(\vec{p}_b + \Delta \vec{p}(\tau), \vec{q}_b, t) - \overline{f_a(\vec{p}_a, \vec{q}_a, t) f_b(\vec{p}_b, \vec{q}_b, t)} \}} d\vec{p}_b \, d\vec{q}_R \quad \text{A.21}$$

It can be shown[2] that

$$\overline{f_a f_b} - \bar{f}_a \bar{f}_b = O(\tau^2) \quad \text{A.22}$$

As mentioned previously, that the collisions are impulsive allows

$$\lim_{\tau \to 0} \left\{ \overline{f_a f_b} - \bar{f}_a \bar{f}_b \right\} = 0 \quad \text{A.23}$$

Thus:

$$\frac{\partial \bar{f}_a}{\partial t} + \frac{p_{ia}}{B_{ia}} \frac{\partial \bar{f}_a}{\partial q_{ia}} + \bar{J}_{ia}^e \frac{\partial \bar{f}_a}{\partial p_{ia}} = \frac{1}{\tau} \iint \left(\bar{f}_a' \bar{f}_b' - \bar{f}_a \bar{f}_b \right) d\vec{p}_b \, d\vec{q}_R \quad \text{A.24}$$

$$\bar{f}_a = \bar{f}_a(\vec{p}_a, \vec{q}_a, t) \qquad \bar{f}_a' = \bar{f}_a'(\vec{p}_a - \Delta \vec{p}(\tau), \vec{q}_a, t)$$

$$\bar{f}_b = \bar{f}_b(\vec{p}_b, \vec{q}_b, t) \qquad \bar{f}_b' = \bar{f}_b'(\vec{p}_b + \Delta \vec{p}(\tau), \vec{q}_b, t) \qquad \text{A.25}$$

APPENDIX B
Equations of Motion During Collision

Without loss of generality, we may locate the origin of our coordinate system at the c.g. of molecule a at the instant of impact. Further, we may also rotate the axis system to align $\vec{x}_a$ with the axis of molecule a. Thus:
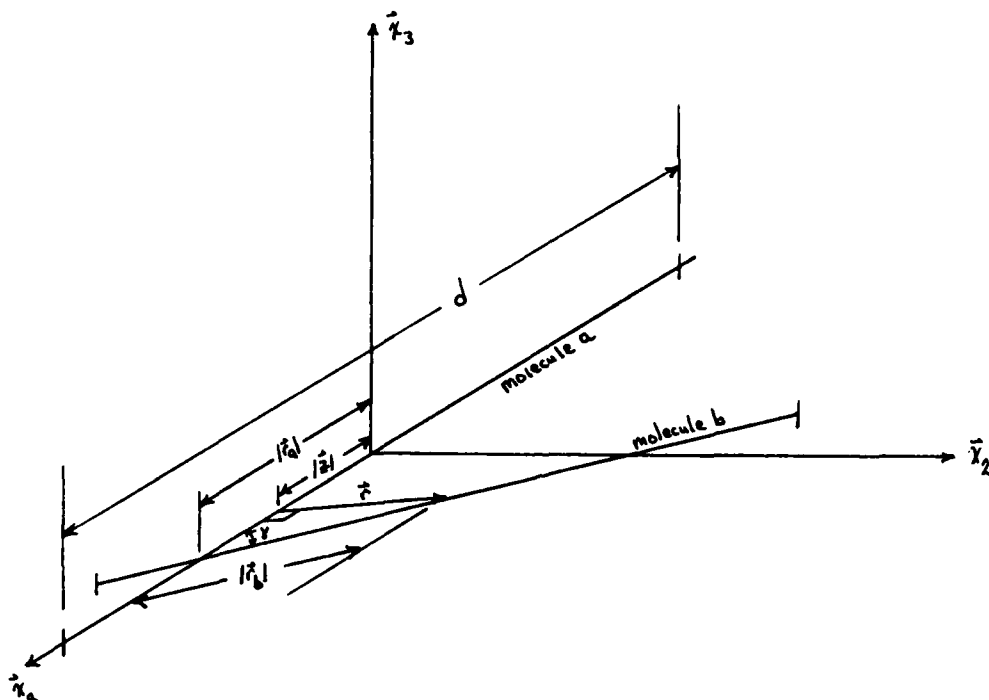
The collision geometry of molecule b with respect to molecule a is uniquely described by the quantities:

$$\vec{r}$$
$$\vec{r}_a$$
$$\vec{r}_b$$
$$\hat{z}$$

where $\vec{r}_b \cdot \hat{i}_a = |\vec{r}_b| \cos \gamma$.

The equations of motion are:

$$m_a' \vec{V}_a' = m_a \vec{V}_a + \vec{J}_a \qquad\qquad B.1$$

$$m_b' \vec{V}_b' = m_b \vec{V}_b + \vec{J}_b \qquad\qquad B.2$$

$$I_a' \dot{\vec{\omega}}_a' = I_a \dot{\vec{\omega}}_a + \vec{r}_a \times \vec{J}_a \qquad\qquad B.3$$

$$I_b' \dot{\vec{\omega}}_b' = I_b \dot{\vec{\omega}}_b + \vec{r}_b \times \vec{J}_b \qquad\qquad B.4$$

$$\vec{J}_a + \vec{J}_b = 0 \qquad\qquad B.5$$

Assume:

i) $\quad m_a' = m_a = m_b' = m_b \equiv m$

ii) $\quad I_a' = I_a = I_b' = I_b \equiv I$

The above assumptions in conjunction with equation B.5
yields

$$m \vec{V}_a' = m \vec{V}_a + \vec{J} \qquad\qquad B.6$$

$$m \vec{V}_b' = m \vec{V}_b - \vec{J} \qquad\qquad B.7$$

$$I \dot{\vec{\omega}}_a' = I \dot{\vec{\omega}}_a + \vec{r}_a \times \vec{J} \qquad\qquad B.8$$

$$I \dot{\vec{\omega}}_b' = I \dot{\vec{\omega}}_b - \vec{r}_b \times \vec{J} \qquad\qquad B.9$$

There are four equations, B.6 through B.9 in five unknowns, $\vec{J}$,
$\vec{V}_a'$, $\vec{V}_b'$, $\vec{\omega}_a'$, $\vec{\omega}_b'$. The fifth equation of motion depends upon the
rod material and surface. The rods shall be assumed to be
perfectly elastic and perfectly smooth. Thus, the components of

the relative velocity tangent to the "collision plane" are unchanged by the collision while the normal component is completely reversed.

The plane of collision is that plane containing the three vectors $\vec{x}_a$, $\vec{r}$ and $\vec{r}_b$. Let the normal unit vector of this plane be denoted as $\hat{i}_N$. The two tangential unit vectors will be denoted $\hat{i}_{T1}$ and $\hat{i}_{T2}$, and where $\hat{i}_{T1}$ is oriented such that $\hat{i}_{T1} \cdot \hat{i}_a = 1$. Thus, the final equations of motion are:

$$\left(\vec{V}_R' \cdot \hat{i}_N\right)\hat{i}_N = -\left(\vec{V}_R \cdot \hat{i}_N\right)\hat{i}_N \qquad \text{B.10}$$

$$\left(\vec{V}_R' \cdot \hat{i}_{T1}\right)\hat{i}_{T1} = \left(\vec{V}_R \cdot \hat{i}_{T1}\right)\hat{i}_{T1} \qquad \text{B.11}$$

$$\left(\vec{V}_R' \cdot \hat{i}_{T2}\right)\hat{i}_{T2} = \left(\vec{V}_R \cdot \hat{i}_{T2}\right)\hat{i}_{T2} \qquad \text{B.12}$$

and the relative velocities before and after collision are:

$$\vec{V}_R = \vec{V}_b - \vec{V}_a + \vec{\omega}_b \times \vec{r}_b - \vec{\omega}_a \times \vec{r}_a \qquad \text{B.13}$$

$$\vec{V}_R' = \vec{V}_b' - \vec{V}_a' + \vec{\omega}_b' \times \vec{r}_b - \vec{\omega}_a' \times \vec{r}_a \qquad \text{B.14}$$

One can now solve for $\vec{J}$, and then $\vec{V}_a'$, $\vec{V}_b'$, $\vec{\omega}_a'$ and $\vec{\omega}_b'$. By equations B.6 through B.9:

$$\vec{V}_a' = \vec{V}_a + \vec{J}/m \; ; \; \vec{V}_b' = \vec{V}_b - \vec{J}/m \; ; \; \vec{\omega}_b' \times \vec{r}_b = \vec{\omega}_b \times \vec{r}_b - \frac{(\vec{r}_b \times \vec{J})}{I} \times \vec{r}_b \; ; \; \vec{\omega}_a' \times \vec{r}_a = \vec{\omega}_a \times \vec{r}_a - \frac{(\vec{r}_a \times \vec{J})}{I} \times \vec{r}_a$$

Thus:

$$\vec{V}_R' = \vec{V}_b - \vec{J}/m - \vec{V}_a - \vec{J}/m + \vec{\omega}_b \times \vec{r}_b - \vec{\omega}_a \times \vec{r}_a - \left[(\vec{r}_b \times \vec{J})\times \vec{r}_b + (\vec{r}_a \times \vec{J})\times \vec{r}_a\right]/I$$

By equation B.13;

$$\vec{V}_R' = \vec{V}_R - \frac{2\vec{J}}{m} + \frac{1}{I}\left[\vec{r}_b \times (\vec{r}_b \times \vec{J}) + \vec{r}_a \times (\vec{r}_a \times \vec{J})\right] \qquad \text{B.15}$$

Substituting equation B.15 into equations B.11 and B.12 shows:

$$0 = \left\{\frac{1}{I}\left[\vec{r}_a \times (\vec{r}_a \times \vec{J}) + \vec{r}_a \times (\vec{r}_a \times \vec{J})\right] - \frac{2}{m}\vec{J}\right\} \cdot \hat{\imath}_{T1} = \left\{\frac{1}{I}\left[\vec{r}_b \times (\vec{r}_b \times \vec{J}) + \vec{r}_a \times (\vec{r}_a \times \vec{J})\right] - \frac{2\vec{J}}{m}\right\} \cdot \hat{\imath}_{T2} \qquad \text{B.16}$$

$$0 = \left\{\frac{1}{I}\left[(\vec{r}_b \cdot \vec{J})\vec{r}_b - |\vec{r}_b|^2\vec{J} + (\vec{r}_a \cdot \vec{J})\vec{r}_a - |\vec{r}_a|^2\vec{J}\right] - \frac{2\vec{J}}{m}\right\} \cdot \hat{\imath}_{T1} =$$

$$\left\{\frac{1}{I}\left[(\vec{r}_b \cdot \vec{J})\vec{r}_b - |\vec{r}_b|^2\vec{J} + (\vec{r}_a \cdot \vec{J})\vec{r}_a - |\vec{r}_a|^2\vec{J}\right] - \frac{2\vec{J}}{m}\right\} \cdot \hat{\imath}_{T2} \qquad \text{B.17}$$

Equations B.16 and B.17 can hold in general only if $\vec{J} \perp \hat{\imath}_{T1}$ and $\vec{J} \perp \hat{\imath}_{T2}$ which also states $\vec{J} \perp \vec{r}_a$ and $\vec{J} \perp \vec{r}_b$. Therefore, $\vec{J} \parallel \hat{\imath}_N$. We have found the direction of $\vec{J}$; now we must find its magnitude. Substituting equation B.15 into equation B.10 yields:

$$\left\{\vec{V}_R - \frac{2\vec{J}}{m} + \frac{1}{I}\left[\vec{r}_a \times (\vec{r}_a \times \vec{J}) + \vec{r}_b \times (\vec{r}_b \times \vec{J})\right]\right\} \cdot \hat{\imath}_N = -\vec{V}_R \cdot \hat{\imath}_N$$

$$\left\{-\frac{2\vec{J}}{m} + \frac{1}{I}\left[\vec{r}_a \times (\vec{r}_a \times \vec{J}) + \vec{r}_b \times (\vec{r}_b \times \vec{J})\right]\right\} \cdot \hat{\imath}_N = -2\vec{V}_R \cdot \hat{\imath}_N$$

Since $\vec{r}_a \cdot \vec{J} = \vec{r}_b \cdot \vec{J} = 0$:

$$\left\{-\frac{2\vec{J}}{m} - \frac{1}{I}\left[|\vec{r}_a|^2\vec{J} + |\vec{r}_b|^2\vec{J}\right]\right\} \cdot \hat{\imath}_N = -2\vec{V}_R \cdot \hat{\imath}_N$$

Since $\vec{J} \cdot \hat{\imath}_N = \pm|\vec{J}|$, define: $\vec{J} \cdot \hat{\imath}_N = |\vec{J}|$ which produces:

$$|\vec{J}| = \left\{\frac{2mI}{2I + m|\vec{r}_a|^2 + m|\vec{r}_b|^2}\right\}\vec{V}_R \cdot \hat{\imath}_N \qquad \text{B.18}$$

Thus:

$$\vec{J} = \left\{\frac{2mI}{2I + m|\vec{r}_a|^2 + m|\vec{r}_b|^2}\right\}(\vec{V}_R \cdot \hat{\imath}_N)\hat{\imath}_N \qquad \text{B.19}$$

Substitution of equation B.19 into equations B.6 through B.9 yields:

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$$m\vec{V}_a' = m\vec{V}_a + \left\{ \frac{2mI}{2I + m|\vec{r}_a|^2 + m|\vec{r}_b|^2} \right\} (\vec{V}_R \cdot \hat{\imath}_N) \hat{\imath}_N \qquad \text{B.20}$$

$$m\vec{V}' = m\vec{V} - \left\{ \frac{2mI}{2I + m|\vec{r}_a|^2 + m|\vec{r}_b|^2} \right\} (\vec{V}_R \cdot \hat{\imath}_N) \hat{\imath}_N \qquad \text{B.21}$$

$$I\vec{\omega}_a' = I\vec{\omega}_a + \left\{ \frac{2mI}{2I + m|\vec{r}_a|^2 + m|\vec{r}_b|^2} \right\} (\vec{V}_R \cdot \hat{\imath}_N)(\vec{r}_a \times \hat{\imath}_N) \qquad \text{B.22}$$

$$I\vec{\omega}_b' = I\vec{\omega}_b - \left\{ \frac{2mI}{2I + m|\vec{r}_a|^2 + m|\vec{r}_b|^2} \right\} (\vec{V}_R \cdot \hat{\imath}_N)(\vec{r}_b \times \hat{\imath}_N) \qquad \text{B.23}$$

The above could just as easily be cast in forms where the primed variables are the initial quantities. From equation B.10 and the definition that $\vec{V}_R' \cdot \hat{\imath}_N$ be positive in sign, the direction of $\hat{\imath}_N$ is reversed for this case. Thus:

$$m\vec{V}_a = m\vec{V}_a' + \left\{ \frac{2mI}{2I + m|\vec{r}_a|^2 + m|\vec{r}_b|^2} \right\} (\vec{V}_R' \cdot \hat{\imath}_N) \hat{\imath}_N \qquad \text{B.24}$$

$$m\vec{V}_b = m\vec{V}_b' - \left\{ \frac{2mI}{2I + m|\vec{r}_a|^2 + m|\vec{r}_b|^2} \right\} (\vec{V}_R' \cdot \hat{\imath}_N) \hat{\imath}_N \qquad \text{B.25}$$

$$I\vec{\omega}_a = I\vec{\omega}_a' + \left\{ \frac{2mI}{2I + m|\vec{r}_a|^2 + m|\vec{r}_b|^2} \right\} (\vec{V}_R' \cdot \hat{\imath}_N)(\vec{r}_a \times \hat{\imath}_N) \qquad \text{B.26}$$

$$I\vec{\omega}_b = I\vec{\omega}_b' - \left\{ \frac{2mI}{2I + m|\vec{r}_a|^2 + m|\vec{r}_b|^2} \right\} (\vec{V}_R' \cdot \hat{\imath}_N)(\vec{r}_b \times \hat{\imath}_N) \qquad \text{B.27}$$

Therefore, given a direct encounter where the initial velocities are $\vec{V}_a$, $\vec{V}_b$, $\vec{\omega}_a$, $\vec{\omega}_b$ and the unit normal of the collision plane is $\hat{i}_N$, there exists an inverse encounter with initial velocities equal to the final velocity of the direct encounter and with a unit normal vector $-\hat{i}_N$ of the collision plane. Other than reversal of the collision plane unit normal vector, the geometry of the two collisions is identical in terms of $\vec{r}$, $\vec{r}_a$, $\vec{r}_b$, and $\vec{z}$.

APPENDIX C

Elemental Five Volume in Spherical Coordinates

By the method of successive projection:

$$x = r\cos\phi \sin\theta \sin\alpha \sin\beta$$
$$y = r\sin\phi \sin\theta \sin\alpha \sin\beta$$
$$z = r\cos\theta \sin\alpha \sin\beta \qquad\qquad \text{C.1}$$
$$a = r\cos\alpha \sin\beta$$
$$b = r\cos\beta$$

$$J = \frac{\partial(x,y,z,a,b)}{\partial(r,\phi,\theta,\alpha,\beta)}$$

$$J =$$

$\cos\phi \sin\theta \sin\alpha \sin\beta$	$-r\sin\phi \sin\theta \sin\alpha \sin\beta$	$r\cos\phi \cos\theta \sin\alpha \sin\beta$	$r\cos\phi \sin\theta \cos\alpha \sin\beta$	$r\cos\phi \sin\theta \sin\alpha \cos\beta$
$\sin\phi \sin\theta \sin\alpha \sin\beta$	$r\cos\phi \sin\theta \sin\alpha \sin\beta$	$r\sin\phi \cos\theta \sin\alpha \sin\beta$	$r\sin\phi \sin\theta \cos\alpha \sin\beta$	$r\sin\phi \sin\theta \sin\alpha \cos\beta$
$\cos\theta \sin\alpha \sin\beta$	0	$-r\sin\theta \sin\alpha \sin\beta$	$r\cos\theta \cos\alpha \sin\beta$	$r\cos\theta \sin\alpha \cos\beta$
$\cos\alpha \sin\beta$	0	0	$-r\sin\alpha \sin\beta$	$r\cos\alpha \cos\beta$
$\cos\beta$	0	0	0	$-r\sin\beta$

$$J=$$

$$
\begin{vmatrix}
r\cos\phi\sin\theta\sin\alpha\sin\beta & r\sin\phi\cos\theta\sin\alpha\sin\beta & r\sin\phi\sin\theta\cos\alpha\sin\beta & \sin\phi\sin\theta\sin\alpha\sin\beta & r\sin\phi\sin\theta\sin\alpha\cos\beta \\[2ex]
-r\sin\phi\sin\theta\sin\alpha\sin\beta & r\cos\phi\cos\theta\sin\alpha\sin\beta & r\cos\phi\sin\theta\cos\alpha\sin\beta & \cos\phi\sin\theta\sin\alpha\sin\beta & r\cos\phi\sin\theta\sin\alpha\cos\beta \\[2ex]
0 & -r\sin\theta\sin\alpha\sin\beta & r\cos\theta\cos\alpha\sin\beta & \cos\theta\sin\alpha\sin\beta & r\cos\theta\sin\alpha\cos\beta \\[2ex]
0 & 0 & -r\sin\alpha\sin\beta & \cos\alpha\sin\beta & r\cos\alpha\cos\beta \\[2ex]
0 & 0 & 0 & \cos\beta & -r\sin\beta
\end{vmatrix}
$$

Combination	Permutation		Sign
$q_{11}q_{22}q_{33}q_{44}q_{55}$	even	0	+
$q_{11}q_{22}q_{33}q_{45}q_{54}$	odd	1	−
$q_{11}q_{22}q_{34}q_{43}q_{55}$	odd	1	−
$q_{11}q_{23}q_{32}q_{44}q_{55}$	odd	1	−
$q_{12}q_{21}q_{33}q_{44}q_{55}$	odd	1	−
$q_{11}q_{22}q_{35}q_{43}q_{54}$	even	2	+
$q_{12}q_{21}q_{33}q_{45}q_{54}$	even	2	+
$q_{12}q_{21}q_{34}q_{43}q_{55}$	even	2	+
$q_{11}q_{23}q_{32}q_{45}q_{54}$	even	2	+
$q_{13}q_{21}q_{32}q_{44}q_{55}$	even	2	+
$q_{11}q_{24}q_{32}q_{43}q_{55}$	even	2	+
$q_{12}q_{21}q_{35}q_{43}q_{54}$	odd	3	−
$q_{13}q_{21}q_{32}q_{45}q_{54}$	odd	3	−
$q_{14}q_{21}q_{32}q_{43}q_{55}$	odd	3	−
$q_{11}q_{25}q_{32}q_{43}q_{54}$	odd	3	−
$q_{15}q_{21}q_{32}q_{43}q_{54}$	even	4	+

$$J = \left[a_{11}a_{22}a_{33}a_{44}a_{55} + a_{11}a_{22}a_{35}a_{43}a_{54} + a_{12}a_{21}a_{33}a_{45}a_{54} + a_{12}a_{21}a_{34}a_{43}a_{55} \right.$$

$$\left. + a_{11}a_{23}a_{32}a_{45}a_{54} + a_{13}a_{21}a_{32}a_{44}a_{55} + a_{15}a_{21}a_{32}a_{43}a_{54} + a_{11}a_{24}a_{32}a_{43}a_{55} \right]$$

$$- \left[a_{11}a_{22}a_{33}a_{45}a_{54} + a_{11}a_{22}a_{34}a_{43}a_{55} + a_{12}a_{21}a_{33}a_{44}a_{55} + a_{11}a_{23}a_{32}a_{44}a_{55} \right.$$

$$\left. + a_{12}a_{21}a_{35}a_{43}a_{54} + a_{11}a_{25}a_{32}a_{43}a_{54} + a_{13}a_{21}a_{32}a_{45}a_{54} + a_{14}a_{21}a_{32}a_{43}a_{55} \right]$$

$$J = -r^4 \cos^2\phi \cos^2\theta \sin\theta \sin^2\alpha \cos^2\alpha \sin^5\beta - r^4 \cos^2\phi \cos^2\theta \sin\theta \sin^4\alpha \sin^3\beta \cos^2\beta$$

$$- r^4 \sin^2\phi \cos^2\theta \sin\theta \sin^2\alpha \cos^2\alpha \sin^3\beta \cos^2\beta - r^4 \sin^2\phi \cos^2\theta \sin\theta \sin^4\alpha \sin^5\beta$$

$$- r^4 \cos^2\phi \sin^3\theta \sin^2\alpha \cos^2\alpha \sin^3\beta \cos^2\beta - r^4 \sin^2\phi \sin^3\theta \sin^2\alpha \cos^2\alpha \sin^5\beta$$

$$- r^4 \sin^2\phi \sin^3\theta \sin^4\alpha \sin^3\beta \cos^2\beta - r^4 \cos^2\phi \sin^3\theta \sin^4\alpha \sin^5\beta$$

$$- r^4 \cos^2\phi \cos^2\theta \sin\theta \sin^2\alpha \cos^2\alpha \sin^3\beta \cos^2\beta - r^4 \cos^2\phi \cos^2\theta \sin\theta \sin^4\alpha \sin^5\beta$$

$$- r^4 \sin^2\phi \cos^2\theta \sin\theta \sin^2\alpha \cos^2\alpha \sin^5\beta - r^4 \cos^2\phi \sin^3\theta \sin^2\alpha \cos^2\alpha \sin^5\beta$$

$$- r^4 \sin^2\phi \cos^2\theta \sin\theta \sin^4\alpha \sin^3\beta \cos^2\beta - r^4 \cos^2\phi \sin^3\theta \sin^4\alpha \sin^3\beta \cos^2\beta$$

$$- r^4 \sin^2\phi \sin^3\theta \sin^2\alpha \cos^2\alpha \sin^3\beta \cos^2\beta - r^4 \sin^2\phi \sin^3\theta \sin^4\alpha \sin^5\beta$$

$$J = -r^4 \left(\sin\theta \sin^2\alpha \cos^2\alpha \sin^5\beta + \sin\theta \sin^4\alpha \sin^3\beta \cos^2\beta + \sin^2\alpha \cos^2\alpha \sin^3\beta \cos^2\beta \sin\theta \right.$$

$$\left. + \sin\theta \sin^4\alpha \sin^5\beta \right)$$

$$J = -r^4 \sin\theta \left(\left[\cos^2\alpha + \sin^2\alpha \right]\left[\sin^2\alpha \sin^5\beta \right] + \left[\cos^2\alpha + \sin^2\alpha \right]\left[\sin^2\alpha \sin^3\beta \cos^2\beta \right] \right)$$

$$J = -r^4 \sin\theta \left(\sin^2\alpha \sin^5\beta + \sin^2\alpha \sin^3\beta \cos^2\beta \right)$$

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$$J = -r^4 \sin\theta \sin^2\alpha \sin^3\beta \qquad \text{C.2}$$

$$dV = |J| \, dr \, d\phi \, d\theta \, d\alpha \, d\beta = dx \, dy \, dz \, da \, db \qquad \text{C.3}$$

$$dV = r^4 \sin\theta \sin^2\alpha \sin^3\beta \, dr \, d\phi \, d\theta \, d\alpha \, d\beta \qquad \text{C.4}$$

$$\iiiint dV = \int_0^\pi \int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^c r^4 \sin\theta \sin^2\alpha \sin^3\beta \, dr \, d\phi \, d\theta \, d\alpha \, d\beta \qquad \text{C.5}$$

$$\iiiint dV = \left(\phi \Big|_0^{2\pi}\right)\left(-\cos\theta \Big|_0^\pi\right)\left(\left(\frac{\alpha}{2} - \frac{\sin 2\alpha}{4}\right)\Big|_0^\pi\right)\left(-\frac{\cos\beta}{3}\Big|_0^\pi\right)\left(\left(\sin^2\beta + 2\right)\Big|_0^\pi\right)\int_0^c r^4 \, dr \qquad \text{C.6}$$

$$\iiiint dV = \frac{8\pi^2}{3}\int_0^r r^4 \, dr \qquad \text{C.7}$$

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APPENDIX D
Integral Identities

Consider the integral

$$\int_{-a}^{+a} \phi(\vec{c}) \, d\vec{c} \qquad\qquad D.1$$

where $\vec{c}$ is the five vector

$$\vec{c} = U\hat{\imath}_x + V\hat{\imath}_y + W\hat{\imath}_z + R\hat{\imath}_\theta + S\hat{\imath}_\phi \qquad\qquad D.2$$

of magnitude C. Let $\phi(C) = F(C) \, U^2$. By symmetry:

$$\int_{-a}^{+a} U^2 F(c) \, d\vec{c} = \int_{-a}^{+a} V^2 F(c) \, d\vec{c} = \int_{-a}^{+a} W^2 F(c) \, d\vec{c} = \int_{-a}^{+a} R^2 F(c) \, d\vec{c} = \int_{-a}^{+a} S^2 F(c) \, d\vec{c}. \qquad D.3$$

Then,

$$\int_{-a}^{+a} U^2 F(c) \, d\vec{c} = \frac{1}{5} \int_{-a}^{+a} (U^2 + V^2 + W^2 + R^2 + S^2) F(c) \, d\vec{c} = \frac{1}{5} \int_{-a}^{+a} c^2 F(c) \, d\vec{c} \qquad D.4$$

and

$$\int_{-a}^{+a} F(c) \, \vec{c}\,\vec{c} \, d\vec{c} = \frac{1}{5} \, \overset{\leftrightarrow}{I} \int_{-a}^{+a} c^2 F(c) \, d\vec{c} \qquad\qquad D.5$$

because the integrals of the non-diagonal terms vanish as they are odd functions of U, V, W, R, or S. Thus

$$\int_{-a}^{+a} F(c) \, \overset{\ast}{\vec{c}}\,\vec{c} \, d\vec{c} = 0. \qquad\qquad D.6$$

For any vector $\vec{A} \neq \hat{\lambda}(\vec{c})$

$$\int_{-a}^{+a} F(c) (\vec{A} \cdot \vec{c}) \vec{c} \, d\vec{c} = \vec{A} \cdot \int_{-a}^{+a} F(c) \, \vec{c}\,\vec{c} \, d\vec{c} \qquad\qquad D.7$$

$$= \frac{1}{5} \, \vec{A} \int_{-a}^{+a} c^2 F(c) \, d\vec{c}. \qquad\qquad D.8$$

Next, let $\phi(C) = S^4 F(C)$. Where $S = C\cos\beta$. Then:

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$$\int_{-c}^{+c} F(C) S^4 d\vec{C} = \int_0^{\pi} \int_0^{\pi} \int_0^{\pi} \int_0^{2\pi} \int_0^{C} F(C) C^4 \cos^4\beta \, C^4 \sin\theta \, \sin^2\alpha \, \sin^3\beta \, dc \, d\phi \, d\theta \, d\alpha \, d\beta \qquad \text{D.9}$$

Then:

$$\int_0^{\pi} \cos^4\beta \, \sin^3\beta \, d\beta = N \int_0^{\pi} \sin^3\beta \, d\beta \qquad \text{D.10}$$

where N is a factor to be determined. Thus:

$$\int_0^{\pi} \cos^4\beta \sin^3\beta \, d\beta = \int_0^{\pi} \cos^4\beta \, (1-\cos^2\beta) \sin\beta \, d\beta = -\frac{1}{5} \cos^5\beta \Big|_0^{\pi} + \frac{1}{7} \cos^7\beta \Big|_0^{\pi} = \frac{4}{35} \qquad \text{D.11}$$

and

$$\int_0^{\pi} \sin^3\beta \, d\beta = -\frac{1}{3} \cos\beta \, (\sin^2\beta + 2) \Big|_0^{\pi} = \frac{4}{3} \qquad \text{D.12}$$

Thus:

$$N = 3/35 \qquad \text{D.13}$$

and:

$$\int_{-c}^{+c} F(C) S^4 d\vec{C} = \frac{3}{35} \int_{-c}^{+c} F(C) C^4 \, d\vec{C}. \qquad \text{D.14}$$

Let $\phi(C) = F(C) R^2 S^2$ where $R = C\cos\alpha\sin\beta$, $S = C\cos\beta$. Then

$$\int_{-c}^{+c} F(C) R^2 S^2 d\vec{C} = \int_0^{\pi} \int_0^{\pi} \int_0^{\pi} \int_0^{2\pi} \int_0^{C} F(C) C^4 \cos^2\alpha \, \cos^2\beta \, \sin^2\beta \, C^4 \sin\theta \, \sin^2\alpha \, \sin^3\beta \, dc \, d\phi \, d\theta \, d\alpha \, d\beta \qquad \text{D.15}$$

and

$$\int_0^{\pi} \int_0^{\pi} \cos^2\alpha \sin^2\alpha \, \cos^2\beta \sin^5\beta \, d\alpha \, d\beta = N \int_0^{\pi} \int_0^{\pi} \sin^2\alpha \sin^3\beta \, d\alpha \, d\beta \qquad \text{D.16}$$

$$= \frac{4N}{3} \int_0^{\pi} \sin^2\alpha \, d\alpha \qquad \text{D.17}$$

$$= \frac{2\pi N}{3} \qquad \text{D.18}$$

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Integrating with respect to β:

$$\int_0^{\pi} \cos^2\beta \sin^5\beta \, d\beta = \int_0^{\pi} \cos^2\beta (1-\cos^2\beta)^2 \sin\beta \, d\beta$$

D.19

$$= \int_0^{\pi} (\cos^2\beta - 2\cos^4\beta + \cos^6\beta) \sin\beta \, d\beta$$

D.20

$$= -\frac{\cos^3\beta}{3}\Big|_0^{\pi} + \frac{2}{5}\cos^5\beta\Big|_0^{\pi} - \frac{1}{7}\cos^7\beta\Big|_0^{\pi}$$

D.21

$$= 16/105$$

D.22

and next with respect to α:

$$\int_0^{\pi} \cos^2\alpha \sin^2\alpha \, d\alpha = \int_0^{\pi} \cos^2\alpha \, d\alpha - \int_0^{\pi} \cos^4\alpha \, d\alpha$$

D.23

$$= \left[\frac{\alpha}{2} + \frac{\sin 2\alpha}{4}\right]_0^{\pi} - \left[\frac{3\alpha}{8} + \frac{\sin 2\alpha}{4} + \frac{\sin 4\alpha}{32}\right]_0^{\pi}$$

D.24

$$= \pi/8$$

D.25

Thus:

$$\frac{2\pi}{105} = \frac{2\pi}{3} \cdot N \quad ; \quad N = 1/35$$

D.26

yielding

$$\int_{-a}^{+a} R^2 S^2 \, F(c) \, d\vec{c} = \frac{1}{35}\int_{-c}^{+c} F(c) c^4 \, d\vec{c}$$

D.27

The integral

$$\int_{-a}^{+a} F(c) \, \vec{c}\vec{c} \, (\vec{c}\vec{c} : \vec{\vec{B}}) \, d\vec{c}$$

D.28

where $\vec{\vec{B}} \neq \vec{\vec{B}}(\vec{c})$ may next be evaluated.

For a typical diagonal element:

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$$\int_{-a}^{+a} F(c)\, u^2 (\vec{c}\vec{c} : \overset{=}{\vec{B}})\, d\vec{c} = \int_{-a}^{+a} F(c)\, u^2 (u^2 \overset{=}{\vec{B}}_{xx} + v^2 \overset{=}{\vec{B}}_{jj} + w^2 \overset{=}{\vec{B}}_{zz} + R^2 \overset{=}{\vec{B}}_{\theta\theta} + S^2 \overset{=}{\vec{B}}_{\phi\phi})\, d\vec{c} \qquad \text{D.29}$$

$$= \left(\tfrac{3}{35} \overset{=}{\vec{B}}_{xx} + \tfrac{1}{35} \overset{=}{\vec{B}}_{jj} + \tfrac{1}{35} \overset{=}{\vec{B}}_{zz} + \tfrac{1}{35} \overset{=}{\vec{B}}_{\theta\theta} + \tfrac{1}{35} \overset{=}{\vec{B}}_{\phi\phi} \right) \int_{-a}^{+a} F(c)\, c^4\, d\vec{c} \qquad \text{D.30}$$

$$= \left(\tfrac{2}{35} \overset{=}{\vec{B}}_{xx} + \tfrac{1}{35} \overset{=}{\vec{I}} : \overset{=}{\vec{B}} \right) \int_{-a}^{+a} F(c)\, c^4\, d\vec{c} \qquad \text{D.31}$$

$$\int_{-a}^{+a} F(c)\, u^2 (\vec{c}\vec{c} : \overset{=}{\vec{B}})\, d\vec{c} = \tfrac{2}{35} \overset{=}{\vec{B}}_{xx} \int_{-a}^{+a} F(c)\, c^4\, d\vec{c} \qquad \text{D.32}$$

while for a typical non-diagonal element

$$\int_{-a}^{+a} F(c)\, RS (\vec{c}\vec{c} : \overset{=}{\vec{B}})\, d\vec{c} = \int_{-a}^{+a} F(c)\, RS (RS \overset{=}{\vec{B}}_{\theta\phi} + SR \overset{=}{\vec{B}}_{\phi\theta})\, d\vec{c} \qquad \text{D.33}$$

$$= 2 \int_{-a}^{+a} F(c)\, R^2 S^2 \overset{=}{\vec{B}}_{\theta\phi}\, d\vec{c} \qquad \text{D.34}$$

$$= \tfrac{2}{35} \overset{=}{\vec{B}}_{\theta\phi} \int_{-a}^{+a} F(c)\, c^4\, d\vec{c} \qquad \text{D.35}$$

Thus:

$$\int_{-a}^{+a} F(c)\, \vec{c}\vec{c} (\vec{c}\vec{c} : \overset{=}{\vec{B}})\, d\vec{c} = \tfrac{2}{35} \overset{=}{\vec{B}} \int_{-a}^{+a} F(c)\, c^4\, d\vec{c} \qquad \text{D.36}$$

Since

$$\vec{c}_1 \vec{c}_1 : \vec{c}_2 \vec{c}_2 - \vec{c}_1 \vec{c}_1 : \vec{c}_2 \vec{c}_2 = \vec{c}_1 \vec{c}_1 : \vec{c}_2 \vec{c}_2 - \tfrac{1}{3} c_1^2 (\overset{=}{\vec{I}} : \vec{c}_2 \vec{c}_2) = (\vec{c}_1 \cdot \vec{c}_2)^2 - \tfrac{1}{3} c_1^2 c_2^2 \qquad \text{D.37}$$

then:

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$$\vec{c}\overset{\circ}{\vec{c}}:\overset{\circ}{\vec{C}}\vec{c} = \frac{4}{5}c^4 \tag{D.38}$$

and

$$\frac{4}{35}\overset{\overset{\circ}{=}}{B}\int_{a}^{+a}F(c)c^4 d\vec{c} \cdot \frac{1}{14}\overset{\overset{\circ}{=}}{B}\int_{-a}^{+a}F(c)(\overset{\circ}{\vec{c}}\vec{c}:\overset{\circ}{\vec{c}}\vec{c})d\vec{c}. \tag{D.39}$$

Therefore:

$$\int_{-a}^{+a}F(c)\overset{\circ}{\vec{c}}\vec{c}(\overset{\circ}{\vec{c}}\vec{c}:\overset{\overset{\circ}{=}}{B})d\vec{c} = \frac{2}{35}\overset{\overset{\circ}{=}}{B}\int_{a}^{+a}F(c)c^4 d\vec{c} = \frac{1}{14}\overset{\overset{\circ}{=}}{B}\int_{-a}^{+a}F(c)(\overset{\circ}{\vec{c}}\vec{c}:\overset{\circ}{\vec{c}}\vec{c})d\vec{c} \tag{D.40}$$

APPENDIX E

Conservation Equations

From the Liouville equation

$$\frac{d_e \bar{f}}{dt} \equiv \frac{\partial \bar{f}}{\partial t} + \frac{P_j}{B_j}\frac{\partial \bar{f}}{\partial q_j} + \mathcal{F}_j \frac{\partial \bar{f}}{\partial p_j} = \left(\frac{\partial \bar{f}}{\partial t}\right)_c \qquad \text{E.1}$$

where $B_j \neq B_j(q_j)$, $\mathcal{F}_j$ is generalized force/torque, and

$$j=1 \Rightarrow x \qquad B_1 = m$$
$$j=2 \Rightarrow y \qquad B_2 = m$$
$$j=3 \Rightarrow z \qquad B_3 = m$$
$$j=4 \Rightarrow \theta \qquad B_4 = I$$
$$j=5 \Rightarrow \phi \qquad B_5 = I\sin^2\theta$$

Let $\Psi(\vec{p},\vec{q},t)$ be any function of the molecular momentum, position, and time. The function may be a scalar, vector, or a tensor function. The rate of change of Ψ per unit "volume" due to collisions is:

$$\int \Psi \frac{d_e \bar{f}}{dt}\, d\vec{p} = n\Delta\bar{\Psi}.$$

But:

$$\int \Psi \frac{d_e \bar{f}}{dt}\, d\vec{p} = \int \Psi \left[\frac{\partial \bar{f}}{\partial t} + \frac{P_j}{B_j}\frac{\partial \bar{f}}{\partial q_j} + \mathcal{F}_j \frac{\partial \bar{f}}{\partial p_j}\right] d\vec{p} \qquad \text{E.2}$$

and, expanding:

$$\int \Psi \frac{\partial \bar{f}}{\partial t}\, d\vec{p} = \frac{\partial}{\partial t}\int \Psi \bar{f}\, d\vec{p} - \int \bar{f}\frac{\partial \Psi}{\partial t}\, d\vec{p} = \frac{\partial n\bar{\Psi}}{\partial t} - n\overline{\frac{\partial \Psi}{\partial t}} \qquad \text{E.3}$$

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$$\int \psi \frac{P_i}{B_j} \frac{\partial f}{\partial q_j} d\vec{p} = \frac{\partial}{\partial q_j} \int \psi \frac{P_i}{B_j} f d\vec{p} - \int \frac{P_i}{B_j} f \frac{\partial \psi}{\partial q_j} d\vec{p} = \frac{\partial}{\partial q_j} \left[\overline{\frac{n P_j \psi}{B_j}} \right] - n \overline{\frac{P_i}{B_j} \frac{\partial \psi}{\partial q_j}} \qquad \text{E.4}$$

since $\vec{p} \neq \vec{p}(\vec{q})$,

$$\int \psi \mathfrak{F}_j \frac{\partial f}{\partial p_j} d\vec{p} = \mathfrak{F}_j \int \psi \frac{\partial f}{\partial p_j} d\vec{p} = \mathfrak{F}_j \left[\psi f \Big|_{-\infty}^{+\infty} - \int f \frac{\partial \psi}{\partial p_j} d\vec{p} \right] = -n \mathfrak{F}_j \overline{\frac{\partial \psi}{\partial p_j}} . \qquad \text{E.5}$$

Giving:

$$n \Delta \overline{\psi} = \frac{\partial n \overline{\psi}}{\partial t} + \frac{\partial}{\partial q_j} \left[\overline{\frac{n P_j \psi}{B_j}} \right] - n \left\{ \overline{\frac{\partial \psi}{\partial t}} + \overline{\frac{P_i}{B_j} \frac{\partial \psi}{\partial q_j}} + \mathfrak{F}_j \overline{\frac{\partial \psi}{\partial p_j}} \right\} . \qquad \text{E.6}$$

If Ψ happens to be a conserved quantity, then $\Delta \bar{\Psi} = 0$. Such
quantities are mass (for non-reacting gases and neglecting
nuclear effects), linear momentum, total angular momentum, and
energy (for non-nuclear effects). These conservation equations
follow.

    i) Conservation of Mass:

Under the above stipulations, this reduces to the conservation of
the number of molecules. Thus, $\Psi = 1$.

Equation E.6 becomes:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial q_j} \left[\overline{\frac{n P_j}{B_j}} \right] = 0 \quad ; \quad j = 1 \to 5 \qquad \text{E.7}$$

B_5 is now $I/2$ for the above equation as this is the number average value of B_5. Next, decompose the momentum, $\vec{p}$, into a peculiar component, $\vec{P}$, and a mean component $\vec{p}_0$. Also, $\vec{P} = \vec{P}(\vec{p},\vec{q},t)$. Therefore:

$$\vec{p} = \vec{p}_0 + \vec{P}$$

E.8

Equation E.4 is thus:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n}{B_j}(P_{0j} + \overline{P}_j)\right] = 0$$

E.9

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n P_{0j}}{B_j}\right] = 0 \quad \text{for} \quad j = 1 \to 5$$

E.10

ii) Conservation of Linear Momentum:

For $i = 1,2,3$, $\Psi_i = P_i$, whereas $\Psi_i = 0$ for $i = 4,5$.

Equation E.6 yields:

$$\frac{\partial n \overline{P}_i}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n \overline{P_i P_j}}{B_j}\right] - n\left\{\overline{\frac{\partial P_i}{\partial t}} + \overline{\frac{P_j}{B_j}\frac{\partial P_i}{\partial q_j}} + \overline{\dot{J}_j \frac{\partial P_i}{\partial P_j}}\right\} = 0 \qquad \text{where } j = 1 \to 5 \quad \text{E.11}$$

Since $\vec{P} = \vec{P}(\vec{p},\vec{q},t)$, then $\vec{p} = \vec{p}(\vec{q},t)$. Thus:

$$\frac{\partial n \overline{P}_i}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n \overline{P_i P_j}}{B_j}\right] - n\,\dot{J}_j\,\delta_{ij} = 0$$

E.12

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$$\frac{\partial n \overline{P_i}}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n \overline{P_i P_j}}{B_j}\right] - n \, \overline{\mathcal{F}_i} = 0 \qquad \text{E.13}$$

$$\frac{\partial n (P_{0i} + \overline{P_i})}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n}{B_j}\overline{(P_{0i} + P_i)(P_{0j} + P_j)}\right] - n \, \overline{\mathcal{F}_i} = 0 \qquad \text{E.14}$$

$$\frac{\partial n P_{0i}}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n}{B_j}\left(P_{0i} P_{0j} + \overline{P_i P_j}\right)\right] - n \, \overline{\mathcal{F}_i} = 0 \qquad \text{E.15}$$

$$P_{0i}\frac{\partial n}{\partial t} + n\frac{\partial P_{0i}}{\partial t} + P_{0i}\frac{\partial}{\partial q_j}\left[\frac{n P_{0i}}{B_j}\right] + \frac{n P_{0j}}{B_j}\frac{\partial}{\partial q_j}[P_{0i}] + \frac{\partial}{\partial q_j}\left[\frac{n \overline{P_i P_j}}{B_j}\right] - n \, \overline{\mathcal{F}_i} = 0 \qquad \text{E.16}$$

By continuity, however,

$$n\frac{\partial P_{0i}}{\partial t} + \frac{n P_{0j}}{B_j}\frac{\partial P_{0i}}{\partial q_j} + \frac{\partial}{\partial q_j}\left[\frac{n \overline{P_i P_j}}{B_j}\right] - n \, \overline{\mathcal{F}_i} = 0 \qquad \text{E.17}$$

$$\text{for } j = 1 \to 5 \; ; \; i = 1,2,3$$

iii)   Conservation of Total Angular Momentum:

$$\Upsilon_k = e_{ijk} r_i P_j \qquad \text{for } i,j,k = 1 \to 3$$

$$\Upsilon_k = P_k \qquad \text{for } k = 4,5$$

Denote Ψ_k as l_k for $k = 1 \to 5$.   Equation E.6 yields:

$$\frac{\partial n \overline{l_i}}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n \overline{P_j l_i}}{B_j}\right] - n\left\{\overline{\frac{\partial l_i}{\partial t}} + \frac{\overline{P_j}}{B_j}\frac{\partial l_i}{\partial q_j} + \overline{\mathcal{F}_j\frac{\partial l_i}{\partial P_j}}\right\} = 0 \qquad \text{E.18}$$

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$$\frac{\partial_n \overline{l_i}}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n \overline{p_j l_i}}{B_j}\right] - n \widetilde{\mathcal{F}_i} \overline{\frac{\partial l_i}{\partial p_j}} = 0 . \qquad \text{E.19}$$

Consider first i = 1,2,3. Then:

$$\epsilon_{klm} q_k \frac{\partial_n \overline{p_l}}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n}{B_j} \epsilon_{klm} \overline{p_j p_l} q_k\right] - n \widetilde{\mathcal{F}_j} \overline{\frac{\partial}{\partial p_j}\left(\epsilon_{klm} q_k p_l\right)} = 0 \qquad \text{E.20}$$

$$\epsilon_{klm} q_k \frac{\partial_n \overline{p_l}}{\partial t} + \epsilon_{klm} q_k \frac{\partial}{\partial q_j}\left[\frac{n}{B_j} \overline{p_j p_l}\right] + \frac{n \overline{p_j p_l}}{B_j} \epsilon_{klm} \frac{\partial q_k}{\partial q_j} - n \epsilon_{klm} q_k \widetilde{\mathcal{F}_j} \frac{\partial p_l}{\partial p_j} = 0 \qquad \text{E.21}$$

$$\epsilon_{klm} q_k \frac{\partial_n \overline{p_l}}{\partial t} + \epsilon_{klm} q_k \frac{\partial}{\partial q_j}\left[\frac{n}{B_j} \overline{p_j p_l}\right] + \epsilon_{klm} \frac{n \overline{p_j p_l}}{B_j} \delta_{ij} - n \epsilon_{klm} q_k \widetilde{\mathcal{F}_j} \delta_{jl} = 0 \qquad \text{E.22}$$

$$\epsilon_{klm} q_k \frac{\partial_n \overline{p_l}}{\partial t} + \epsilon_{klm} q_k \frac{\partial}{\partial q_j}\left[\frac{n \overline{p_j p_l}}{B_j}\right] + \epsilon_{klm} \frac{n \overline{p_k p_l}}{B_k} - n \epsilon_{klm} q_k \widetilde{\mathcal{F}_l} = 0 \qquad \text{E.23}$$

$$\text{But,} \quad \overline{p_h p_l} = \overline{p_l p_h} , \quad \text{so:} \qquad \text{E.24}$$

$$\epsilon_{klm} q_k \frac{\partial_n \overline{p_l}}{\partial t} + \epsilon_{klm} q_k \frac{\partial}{\partial q_j}\left[\frac{n \overline{p_j p_l}}{B_j}\right] - n \epsilon_{klm} q_k \widetilde{\mathcal{F}_l} = 0 \qquad \text{E.25}$$

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which the conservation of linear momentum crossed with the position vector. Thus, for i = 1,2,3, the conservation of total angular momentum equation is redundant.

For i = 4,5, $l_i = p_i$ and by the development of the conservation of linear momentum equation:

$$n\frac{\partial \rho_{oi}}{\partial t} + \frac{n\rho_{oj}}{B_j}\frac{\partial \rho_{oi}}{\partial q_j} + \frac{\partial}{\partial q_j}\left[\frac{n\overline{P_i P_j}}{B_j}\right] = 0 \qquad \text{E.26}$$

where one must remember i = 4,5.

iv) Conservation of Energy:

Now: $\qquad \Psi = P_{ii}^2/2B_i$

Equation E.6 yields:

$$\frac{1}{2B_i}\frac{\partial n\overline{P_{ii}^2}}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n\overline{P_j P_{ii}^2}}{2B_j B_i}\right] - n\left\{\frac{1}{2B_i}\frac{\overline{\partial P_{ii}^2}}{\partial t} + \frac{\overline{P_j}}{B_j}\frac{\partial}{\partial q_j}\left[\frac{P_{ii}^2}{2B_i}\right] + \overline{\mathfrak{I}_j}\frac{\partial}{\partial P_j}\left[\frac{P_{ii}^2}{2B_i}\right]\right\} = 0 \qquad \text{E.27}$$

$$\frac{1}{2B_i}\frac{\partial n\overline{P_{ii}^2}}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n\overline{P_j P_{ii}^2}}{2B_j B_i}\right] - n\left\{\frac{1}{2B_i}\frac{\overline{\partial P_{ii}^2}}{\partial t} + \frac{\overline{P_j}}{B_j}\frac{\partial}{\partial q_j}\left[\frac{P_{ii}^2}{2B_i}\right] + \overline{\mathfrak{I}_j\frac{P_i}{B_i}}\right\} = 0. \qquad \text{E.28}$$

Also:

$$\overline{P_j P_{ii}^2} = \overline{(\rho_{oj} + P_j)(\rho_{oi} + P_i)(\rho_{oi} + P_i)} = \overline{(\rho_{oj} + P_j)(\rho_{oii}^2 + 2\rho_{oi}P_i + P_{ii}^2)}$$

$$= \rho_{oj}\rho_{oii}^2 + 2\rho_{oj}\rho_{oi}\overline{P_i} + \rho_{oj}\overline{P_{ii}^2} + \rho_{oii}^2\overline{P_j} + 2\rho_{oi}\overline{P_i P_j} + \overline{P_j P_{ii}^2}$$

$$= \rho_{oj}\rho_{oii}^2 + \rho_{oj}\overline{P_{ii}^2} + 2\rho_{oi}\overline{P_i P_j} + \overline{P_j P_{ii}^2} \qquad \text{E.29}$$

$$\overline{P_{ii}^2} = \overline{P_{oii}^2} + 2p_{oi}\overline{P_i} + \overline{P_{ii}^2} = P_{oii}^2 + \overline{P_{ii}^2} \qquad \text{E.30}$$

$$\frac{\partial \overline{P_{ii}^2}}{\partial \alpha} = 2\overline{P_i}\frac{\partial \overline{P_i}}{\partial \alpha} \qquad \text{where} \quad P_i = P_i(\alpha). \qquad \text{E.31}$$

Thus:

$$\left\{ \frac{\overline{P_i}}{B_i}\frac{\partial n\overline{P_i}}{\partial t} + \frac{\overline{P_i}}{B_i}\frac{\partial}{\partial q_j}\left[\frac{n\overline{P_j P_i}}{B_j}\right] - \frac{\overline{P_i}}{B_i}n\tilde{J}_i \right\} - n\left\{ \frac{1}{2B_i}\overline{\frac{\partial P_{ii}^2}{\partial t}} + \frac{\overline{P_j}}{B_j}\frac{\partial}{\partial q_j}\overline{\left[\frac{P_{ii}^2}{2B_i}\right]} \right\} = 0. \qquad \text{E.32}$$

By the conservation of linear momentum and total angular momentum equations:

$$\frac{\overline{P_i}}{B_i}\frac{\partial n\overline{P_i}}{\partial t} + \frac{\overline{P_i}}{B_i}\frac{\partial}{\partial q_j}\left[\frac{n\overline{P_j P_i}}{B_j}\right] - \frac{\overline{P_i}}{B_i}n\tilde{J}_i = 0 = \frac{1}{2B_i}\frac{\partial n\overline{P_{ii}^2}}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n\overline{P_j P_{ii}^2}}{2B_j B_i}\right] - n\tilde{J}_i\frac{\overline{P_i}}{B_i} \qquad \text{E.33}$$

$$n\left\{ \frac{1}{2B_i}\overline{\frac{\partial P_{ii}^2}{\partial t}} + \frac{\overline{P_j}}{B_j}\frac{\partial}{\partial q_j}\overline{\left[\frac{P_{ii}^2}{2B_i}\right]} \right\} = 0 \qquad \text{E.34}$$

Consider equation E.33 first.

$$\frac{1}{2B_i}\frac{\partial n(P_{oii}^2 + \overline{P_{ii}^2})}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n}{2B_j B_i}\left(P_{oj}P_{oii}^2 + P_{oj}\overline{P_{ii}^2} + \overline{P_j P_{ii}^2} + 2p_{oi}\overline{P_i P_j}\right)\right] - n\tilde{J}_i\frac{P_{oi}}{B_i} = 0 \qquad \text{E.35}$$

$$\frac{1}{2B_i}\frac{\partial n P_{oii}^2}{\partial t} + \frac{\partial}{\partial q_j}\left[\frac{n}{2B_j B_i}\left(P_{oj}P_{oii}^2 + P_{oj}\overline{P_{ii}^2} + \overline{P_j P_{ii}^2} + 2p_{oi}\overline{P_i P_j}\right)\right] - n\tilde{J}_i\frac{P_{oi}}{B_i} + \frac{1}{2B_i}\frac{\partial n\overline{P_{ii}^2}}{\partial t} = 0 \qquad \text{E.36}$$

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$$\frac{1}{2B_i}\left\{ n\frac{d\overline{P_{0ii}^2}}{dt} + \overline{P_{0ii}^2}\frac{dn}{dt}\right\} + \frac{nP_{0j}}{B_j}\frac{d}{dq_j}\left[\frac{\overline{P_{0ii}^2}}{2B_i}\right] + \frac{\overline{P_{0ii}^2}}{2B_i}\frac{d}{dq_j}\left[\frac{nP_{0j}}{B_j}\right] + \frac{d}{dq_j}\left[\frac{n}{2B_iB_j}\left(P_{0j}\overline{P_{ii}^2} + \overline{P_j\,P_{ii}^2} + 2P_{0i}\overline{P_i\,P_j}\right)\right] \quad \text{E.37}$$

$$+ \frac{1}{2B_i}\frac{dn\overline{P_{ii}^2}}{dt} - n\,\mathcal{J}_i\frac{P_{0i}}{B_i} = 0.$$

By the conservation of mass, the above reduces to:

$$\frac{n}{2B_i}\frac{d\overline{P_{0ii}^2}}{dt} + \frac{nP_{0j}}{B_j}\frac{d}{dq_j}\left[\frac{\overline{P_{0ii}^2}}{2B_i}\right] + \frac{d}{dq_j}\left[\frac{n}{2B_jB_i}\left(P_{0j}\overline{P_{ii}^2} + \overline{P_j\,P_{ii}^2} + 2P_{0i}\overline{P_i\,P_j}\right)\right] - n\,\mathcal{J}_i\frac{P_{0i}}{B_i} \quad \text{E.38}$$

$$+ \frac{1}{2B_i}\frac{dn\overline{P_{ii}^2}}{dt} = 0.$$

But $\quad \overline{P_{0ii}^2}/2B_i \quad = \frac{5kT}{2}$.   Thus

$$\frac{5}{2}nk\left[\frac{dT}{dt} + \frac{P_{0j}}{B_j}\frac{dT}{dq_j}\right] + \frac{d}{dq_j}\left[\frac{n}{2B_jB_i}\left(P_{0j}\overline{P_{ii}^2} + \overline{P_j\,P_{ii}^2} + 2P_{0i}\overline{P_i\,P_j}\right)\right] - n\,\mathcal{J}_i\frac{P_{0i}}{B_i} + \frac{1}{2B_i}\frac{dn\overline{P_{ii}^2}}{dt} = 0. \quad \text{E.39}$$

By the assumption of molecular chaos $\frac{d\overline{P_{ii}^2}}{dt} = 0$.   Expanding the last term yields

$$\frac{1}{2B_i}\frac{dn\overline{P_{ii}^2}}{dt} = \frac{1}{2B_i}\left[n\frac{d\overline{P_{ii}^2}}{dt} + \overline{P_{ii}^2}\frac{dn}{dt}\right] = \frac{\overline{P_{ii}^2}}{2B_i}\frac{dn}{dt}. \quad \text{E.40}$$

Thus:

$$\frac{5}{2}nk\left[\frac{dT}{dt} + \frac{P_{0j}}{B_j}\frac{dT}{dq_j}\right] + \frac{\overline{P_{ii}^2}}{2B_i}\frac{dn}{dt} + \frac{\overline{P_{ii}^2}}{2B_i}\frac{d}{dq_j}\left[\frac{nP_{0j}}{B_j}\right] + \frac{nP_{0j}}{B_j}\frac{d}{dq_j}\left[\frac{\overline{P_{ii}^2}}{2B_i}\right]$$

$$+ \frac{d}{dq_j}\left[\frac{n}{2B_jB_i}\left(\overline{P_j\,P_{ii}^2} + 2P_{0i}\overline{P_i\,P_j}\right)\right] - n\,\mathcal{J}_i\frac{P_{0i}}{B_i} = 0. \quad \text{E.41}$$

Again, by the assumption of molecular chaos $\frac{d\overline{P_{ii}^2}}{dq_j} = 0$.   In combination with the conservation of mass equations, this yields:

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$$\frac{5}{2}nk\left[\frac{\partial T}{\partial t} + \frac{P_{0j}}{B_j}\frac{\partial T}{\partial q_j}\right] + \frac{\partial}{\partial q_j}\left[\frac{n}{2B_j B_i}\left(\overline{P_j P_{ii}^2} + 2P_{0i}\overline{P_i P_j}\right)\right] - n\mathcal{J}_i\frac{P_{0i}}{B_i} = 0 \qquad \text{E.42}$$

$$\frac{5}{2}nk\left[\frac{\partial T}{\partial t} + \frac{P_{0j}}{B_j}\frac{\partial T}{\partial q_j}\right] + \frac{\partial}{\partial q_j}\left[\frac{n\overline{P_j P_{ii}^2}}{2B_j B_i}\right] + \left[\frac{n\overline{P_i P_j}}{B_j}\right]\frac{\partial}{\partial q_j}\left[\frac{P_{0i}}{B_i}\right] + \left[\frac{P_{0i}}{B_i}\right]\frac{\partial}{\partial q_j}\left[\frac{n\overline{P_i P_j}}{B_j}\right] - n\mathcal{J}_i\frac{P_{0i}}{B_i} = 0 \quad \text{E.43}$$

$$\frac{5}{2}nk\left[\frac{\partial T}{\partial t} + \frac{P_{0j}}{B_j}\frac{\partial T}{\partial q_j}\right] + \frac{\partial}{\partial q_j}\left[\frac{n\overline{P_j P_{ii}^2}}{2B_j B_i}\right] + \left[\frac{n\overline{P_i P_j}}{B_j}\right]\frac{\partial}{\partial q_j}\left[\frac{P_{0i}}{B_i}\right] + \frac{P_{0i}}{B_i}\left\{\frac{\partial}{\partial q_j}\left[\frac{n\overline{P_j P_i}}{B_j}\right] - n\mathcal{J}_i\right\} = 0. \quad \text{E.44}$$

Next, consider equation E.34.

$$n\left\{\frac{1}{2B_i}\frac{\partial\overline{P_{ii}^2}}{\partial t} + \overline{\frac{P_i}{B_i}\frac{\partial}{\partial q_j}\left[\frac{P_{ii}^2}{2B_i}\right]}\right\} = 0 = n\left\{\frac{1}{2B_i}\left[\frac{\partial P_{0ii}^2}{\partial t} + \overline{\frac{\partial P_{ii}^2}{\partial t}}\right] + \frac{P_{0i}}{B_j}\frac{\partial}{\partial q_j}\left[\frac{P_{0ii}^2}{2B_i}\right]\right.$$

$$\left. + \frac{P_{0i}}{B_j}\overline{\frac{\partial}{\partial q_j}\left[\frac{P_{ii}^2}{2B_i}\right]} + \overline{\frac{P_j}{B_j}\frac{\partial}{\partial q_j}\left[\frac{P_{0ii}^2}{2B_i}\right]} + \overline{\frac{P_j}{B_j}\frac{\partial}{\partial q_j}\left[\frac{P_{ii}^2}{2B_i}\right]}\right\}. \qquad \text{E.45}$$

By the assumption of molecular chaos, this reduces to:

$$n\left\{\frac{1}{2B_i}\frac{\partial P_{0ii}^2}{\partial t} + \frac{P_{0i}}{B_j}\frac{\partial}{\partial q_j}\left[\frac{P_{0ii}^2}{2B_i}\right] + \overline{\frac{P_j}{B_j}\frac{\partial}{\partial q_j}\left[\frac{P_{ii}^2}{2B_i}\right]}\right\} = 0. \qquad \text{E.46}$$

Expanding:

$$n\left\{\frac{P_{0i}}{B_i}\frac{\partial P_{0i}}{\partial t} + \frac{P_{0i}P_{0j}}{B_i B_j}\frac{\partial P_{0i}}{\partial q_j} + \overline{\frac{P_i P_j}{B_i B_j}\frac{\partial P_i}{\partial q_j}}\right\} = 0 \qquad \text{E.47}$$

By molecular chaos, we have:

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$$\frac{P_{oi}}{B_i} \left\{ n \frac{\partial P_{oi}}{\partial t} + \frac{n P_{oj}}{B_j} \frac{\partial P_{oi}}{\partial q_j} \right\} = 0 \qquad\qquad \text{E.48}$$

Adding equations E.44 and E.48 yields:

$$\frac{5}{2} n k \left[\frac{\partial T}{\partial t} + \frac{P_{oj}}{B_j} \frac{\partial T}{\partial q_j} \right] + \frac{\partial}{\partial q_j} \left[\frac{n \overline{P_j' P_{ii}'^2}}{2 B_j B_i} \right] + \left[\frac{n \overline{P_i' P_j'}}{B_j} \right] \frac{\partial}{\partial q_j} \left[\frac{P_{oi}}{B_i} \right]$$

$$\qquad\qquad \text{E.49}$$

$$+ \frac{P_{oi}}{B_i} \left\{ n \frac{\partial P_{oi}}{\partial t} + \frac{n P_{oj}}{B_j} \frac{\partial P_{oi}}{\partial q_j} + \frac{\partial}{\partial q_j} \left[\frac{n \overline{P_i' P_j'}}{B_j} \right] - n \breve{\mathcal{F}}_i \right\} = 0.$$

which by the conservation of linear momentum and total angular momentum yields:

$$\frac{5}{2} n k \left[\frac{\partial T}{\partial t} + \frac{P_{oj}}{B_j} \frac{\partial T}{\partial q_j} \right] + \frac{\partial}{\partial q_j} \left[\frac{n \overline{P_j' P_{ii}'^2}}{2 B_j B_i} \right] + \left[\frac{n \overline{P_i' P_j'}}{B_j} \right] \frac{\partial}{\partial q_j} \left[\frac{P_{oi}}{B_i} \right] = 0. \qquad \text{E.50}$$

APPENDIX F
The Equilibrium Distribution Function

By Enskog's expansion method

$$\mathcal{D}^{\circ} = 0$$

which leads to

$$\left(\frac{\partial \bar{f}}{\partial t}\right)_c = 0 = \iint \left(\bar{f}^{\circ'} \bar{f}_b^{\circ'} - \bar{f}^{\circ} \bar{f}_b^{\circ} \right) |\vec{V}_R| \, d\vec{q}_R \, d\vec{p}_b \qquad \text{F.1}$$

where

$$|d\vec{q}_R| = r^3 \sin\theta \sin^2\alpha \, dr \, d\varphi \, d\theta \, d\alpha \qquad \text{F.2}$$

The only difference between the above collision integral and the collision integral for spherical molecules is the dimensional rank of the vectors $d\vec{q}_R$ and $d\vec{p}_b$. Boltzmann's H-theorem is rank independent and therefore holds for equation F.2. Thus,

$$\bar{f}^{\circ'} \bar{f}_b^{\circ'} = \bar{f}^{\circ} \bar{f}_b^{\circ} \qquad \text{F.3}$$

or

$$\ln \bar{f}^{\circ'} + \ln \bar{f}_b^{\circ'} = \ln \bar{f}^{\circ} + \ln \bar{f}_b^{\circ} \qquad \text{F.4}$$

Since $\ln \bar{f}^{0}$ is both a scalar and a conserved property of the gas, $\ln \bar{f}^{0}$ must be a linear combination of the four conserved properties Ψ^i, $i = 1 \to 4$, such that

$$\ln \bar{f}^{\circ} = \beta^{1,\circ} + \beta_m^{2,\circ} p_m + \beta_k^{3,\circ} v_i p_i + \beta^{4,\circ} p_{ii} / 2 B_i \qquad \text{F.5}$$

for $m = 1 \to 3$; $i,j,k,1 = 1 \to 5$ and where

$$\alpha_i = \epsilon_{jik} r_j \quad \text{for} \quad i,j,k : 1 \rightarrow 3 \tag{F.6}$$

$$\alpha_i = \hat{e}_i \quad \text{for} \quad i:4,5$$

$\beta^{1,0}$ and $\beta^{4,0}$ are scalars, $\beta^{2,0}$ is a three vector, and $\beta^{3,0}$ is a five vector. Define:

$$\beta_i^{5,0} = \epsilon_{jki} \beta_j^{3,0} r_k \quad \text{for} \quad i,j,k : 1 \rightarrow 3$$

$$\beta_i^{5,0} = \beta_i^{3,0} \quad \text{for} \quad i:4,5 \tag{F.7}$$

so that equation F.5 becomes

$$\ln \bar{f}^0 = \beta^{1,0} + \beta_m^{2,0} p_m + \beta_i^{5,0} p_i + \beta^{4,0} p_{ii}^2 / 2\beta_i \tag{F.8}$$

Equation F.8 may be recast as:

$$\ln \bar{f}^0 = \ln \alpha^{(0)} + \frac{\beta^{4,0}}{2\beta_i} \left[p_i - (\beta_i^{5,0} + \beta_i^{2,0})/\beta^{4,0} \right]^2 \tag{F.9}$$

where $\beta_4^{2,0} = \beta_5^{2,0} = 0$. Thus:

$$\bar{f}^0 = \alpha^{(0)} \exp \left\{ \frac{\beta^{4,0}}{2\beta_i} \left[p_i - (\beta_i^{5,0} + \beta_i^{2,0})/\beta^{4,0} \right]^2 \right\} \tag{F.10}$$

Define:

$$X_i \equiv p_i - (\beta_i^{5,0} + \beta_i^{2,0})/\beta^{4,0} \tag{F.11}$$

By Enskog's method, the average value of momentum is defined as:

$$n\vec{p}_0 = \int \vec{p} \, \bar{f}^0 d\vec{p} \tag{F.12}$$

Substituting equations F.10 and F.11 into equation F.12 yields

$$n\vec{p}_0 = \int (\vec{X} + (\vec{\beta}^{5,0} + \vec{\beta}^{2,0})/\beta^{4,0}) \, \alpha^{(0)} \exp\left(\frac{\beta^{4,0}}{2B_i} X_{ii}^2\right) d\vec{X} \qquad \text{F.13}$$

$$n\vec{p}_0 = \int \vec{X} \alpha^{(0)} \exp\left(\frac{\beta^{4,0}}{2B_i} X_{ii}^2\right) d\vec{X} + \frac{\alpha^{(0)}}{\beta^{4,0}} \int (\beta^{5,0} + \beta^{2,0}) \exp\left(\frac{\beta^{4,0}}{2B_i} X_{ii}^2\right) d\vec{X}. \qquad \text{F.14}$$

Thus, we must have:

$$\beta^{4,0} \equiv -\alpha^{(1)}$$

for any of the integrals to be finite. Further, the first

integral vanishes because its integrand is an odd function of $\vec{X}$.

Thus:

$$n\vec{p}_0 = \frac{\alpha^{(0)}}{\beta^{4,0}} \int (\vec{\beta}^{5,0} + \vec{\beta}^{2,0}) \exp\left(\frac{-\alpha^{(1)}}{2B_i} X_{ii}^2\right) d\vec{X} \qquad \text{F.15}$$

or:

$$n\vec{p}_0 = \frac{\alpha^{(0)}}{\beta^{2,0}} (\vec{\beta}^{5,0} + \vec{\beta}^{2,0}) \int \exp\left(\frac{-\alpha^{(1)}}{2B_i} X_{ii}^2\right) d\vec{X} \qquad \text{F.16}$$

However, by definition:

$$n = \alpha^{(0)} \int \exp\left(\frac{-\alpha^{(1)}}{2B_i} X_{ii}^2\right) d\vec{X} \qquad \text{F.17}$$

which leads to

$$\vec{p}_0 = (\vec{\beta}^{5,0} + \vec{\beta}^{2,0})/\beta^{4,0} \qquad \text{F.18}$$

Thus, equation F.11 becomes

$$X_i = P_i - P_{0i}. \qquad \text{F.19}$$

Therefore, X_i is the ith component of the peculiar momentum, or:

$$P_i = X_i \qquad \text{F.20}$$

Therefore: $$\bar{f}^{\,0} = \alpha^{(0)} \exp\left(\frac{-\alpha^{(1)}}{2B_i} P_{ii}^2\right)$$ F.21

Now: $$n = \alpha^{(0)} \int \exp\left(\frac{-\alpha^{(1)}}{2B_i} P_{ii}^2\right) d\vec{P}$$ F.22

From Appendix C: $$n = \frac{8\pi^2 \alpha^{(0)}}{3} \int_0^\infty r^4 e^{-ar^2} dr$$ F.23

where $a = \alpha^{(1)}/2B$ F.24

Consecutively let: $$m = r^2$$ F.25
$$x = am$$ F.26

then F.27
$$n = \frac{8\pi^2 \alpha^{(0)}}{3} a^{-5/2} \int_0^\infty x^{3/2} e^{-x} dx$$

$$n = \frac{8\pi^2 \alpha^{(0)}}{3} a^{-5/2} \Gamma(5/2)$$ F.28

$$n = \alpha^{(0)} \left[\frac{2\pi B}{\alpha^{(1)}}\right]^{5/2}$$ F.29

Finally, the temperature shall be defined as:

$$\frac{5}{2} kT = P_{ii}^2/2B_i$$ F.30

This is the usual kinetic theory definition of temperature. Thus:

$$\frac{5}{2} nkT = \frac{1}{2B_i} \int P_{ii}^2 \bar{f}^{\,0} d\vec{P}$$ F.31

$$\frac{5}{2} nkT = \frac{1}{2B_i} \int P_{ii}^2 \bar{f}^{\,0} d\vec{P}$$ F.32

which by Appendix C may be recast as:

$$S_n kT = \frac{8\pi^2}{3B} \int_0^\infty P^6 \bar{f}^0 dP \qquad \text{F.33}$$

Thus, when the values of $\bar{f}^0$ and $\alpha^{(0)}$ are substituted into the above,

$$SkT = \left(\frac{8\pi^2}{3B}\right)\left(\frac{\alpha^{(1)}}{2\pi B}\right)^{5/2} \int_0^\infty P^6 e^{-\alpha P^2} dP \qquad \text{F.34}$$

$$\text{where } a = \alpha^{(1)}/2B \qquad \text{F.35}$$

In succession, let:

$$y = P^2 \qquad \text{F.36}$$

$$x = ay \qquad \text{F.37}$$

then

$$SkT = \left(\frac{8\pi^2}{6B}\right)\left(\frac{\alpha^{(1)}}{2\pi B}\right)^{5/2} a^{-7/2} \int_0^\infty x^{5/2} e^{-x} dx \qquad \text{F.38}$$

$$SkT = \left(\frac{4}{3B}\right)\left(\frac{1}{\alpha^{(0)}}\right) \frac{1}{\sqrt{\pi}} 2B \Gamma(1/2) \qquad \text{F.39}$$

Thus:

$$\alpha^{(0)} = 1/kT \qquad \text{F.40}$$

and $\bar{f}^0$ is:

$$\bar{f}^0 = n(2\pi kTB_{ii})^{-5/2} e^{-P_{ii}^2/2B_i kT} \qquad \text{F.41}$$

or:

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$$\overline{f}^{\circ} = n \prod_{i=1}^{5} (2\pi kTB_i)^{-1/2} e^{-P_i^2/2B_i kT}$$

F.42

APPENDIX G

Derivation of the Thermodynamic Properties of a Diatomic Gas

The desired equilibrium properties are calculated from the partition function of the gas. Partition functions exist, however, only when energy is quantized. They are, therefore, outside the slope of classical mechanics. This is a problem with classical mechanics as a whole and is not peculiar to the present analysis. Therefore, the works of others shall be followed by assuming a classical partition function exists and is defined by:

$$Z = \frac{1}{h^q} \iint e^{-P_{ii}^2/2B_i kT} d\vec{q} \, d\vec{p} \qquad \text{G.1}$$

For the present case of a diatomic gas, g is five. Thus:

$$Z = \frac{1}{h^5} \iint e^{-P_{ii}^2/2B_i kT} d\vec{p} \, d\vec{q} \qquad \text{G.2}$$

$$= \frac{V}{h^5} \int e^{-P_{ii}^2/2B_i kT} d\vec{p} \qquad \text{G.3}$$

where V is the five-space volume. Using the results of Appendix F, the classical partition function is:

$$Z = V \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \left(\frac{2\pi I kT}{h^2} \right) \qquad \text{G.4}$$

The specific heat at constant volume and the specific heat at constant pressure are derived from:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V \qquad \text{G.5}$$

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$$C_p = C_v + Nk \qquad \text{G.6}$$

where U is the internal energy of the gas. The internal energy may be expressed in terms of the classical partition function as

$$u = \frac{NkT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_v \qquad \text{G.7}$$

Thus:
$$u = \frac{NkT^2}{T^{5/2}} \cdot \frac{5}{2} T^{3/2} = \frac{5}{2} NkT \qquad \text{G.8}$$

which yields
$$C_v = \frac{5}{2} Nk \qquad \text{G.9}$$

and
$$C_p = \frac{7}{2} Nk \qquad \text{G.10}$$

for the equilibrium specific heats. The ratio of specific heats is:

$$\gamma = \frac{C_p}{C_v} = 1.400 \qquad \text{G.11}$$

Expressed in terms of the classical partition function, the specific entropy is:

$$S = Nk\left[1 + \ln\left|\frac{Z}{N}\right| + \frac{T}{Z}\left(\frac{\partial Z}{\partial T}\right)_v\right] \qquad \text{G.12}$$

Thus, substituting for Z yields:

$$S = Nk\left[1 + \ln\left|\left(\frac{2\pi kT}{h^2}\right)^{5/2} m^{3/2} \frac{TV}{N}\right| + \frac{5}{2}\right] \qquad \text{G.13}$$

The volume in five space may be expressed as the product of two volumes

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$$V = V_3 V_2 \qquad\qquad G.14$$

where V_3 is the typical three-space volume and V_2 is the two-space 'volume' of the angular coordinates θ and ϕ. Thus, equation G.13 is:

$$S = Nk\left[\frac{7}{2} + \ln\left|\left(\frac{2\pi m kT}{h^2}\right)^{3/2} \frac{V_3}{N}\right| + \ln\left|\frac{2\pi I kT V_2}{h^2}\right| \right] \qquad G.15$$

The volume, V_2, is simply 4π – the solid angle of a sphere. Thus:

$$S = Nk\left[\frac{7}{2} + \ln\left|\left(\frac{2\pi m kT}{h^2}\right)^{3/2} \frac{V_3}{N}\right| + \ln\left|\frac{8\pi^2 I kT}{h^2}\right| \right] \qquad G.16$$

As known from quantum mechanics, G.16 is correct for a gas composed of heteronuclear, rigid-rotor molecules. Quantum mechanics predicts that in general

$$S = Nk\left[\frac{7}{2} + \ln\left|\left(\frac{2\pi m kT}{h^2}\right)^{3/2} \frac{V_3}{N}\right| + \ln\left|\frac{8\pi^2 I kT}{\sigma h^2}\right| \right] \qquad G.17$$

where σ is the symmetry number such that:

> $\sigma = 1$ for heteronuclear molecule
> $\sigma = 2$ for homonuclear molecules.

The symmetry number arises out of the requirement that the wave function of a homonuclear molecule possesses a certain symmetry with respect to the interchange of the nuclei of the molecule. Classically, the symmetry number ensures that one orientation identical to another orientation does not contribute to the entropy. A rigid rotor, for example, has identical orientations

for $\theta = \pi$, $\phi = \pi$, and $\theta = \pi$, $\phi = 2\pi$. Equation G.17 predicted
the values of the specific entropy given in Table 1 of the text.

APPENDIX H
Development of the Second Term of the Expansion
of the Distribution Function

Since $\bar{f}$ can be expressed as a function of P_i, q_i, and t, the Boltzmann-type equation may be recast as:

$$\mathcal{D}\bar{f} = \frac{D\bar{f}}{Dt} + \delta_{ij}\left[\bar{J}_i^e - \frac{D_{P_{ai}}}{Dt}\right]\frac{\partial\bar{f}}{\partial P_i} + \frac{P_j}{B_j}\frac{\partial\bar{f}}{\partial q_j} - \frac{P_j}{B_j}\frac{\partial\bar{f}}{\partial P_i}\frac{\partial P_{ai}}{\partial q_j} = \left(\frac{\partial\bar{f}}{\partial t}\right)_c \qquad \text{H.1}$$

The Enskog expansion of $\mathcal{D}'$ yields

$$\mathcal{D}\bar{f}' = \frac{D_0\bar{f}^\circ}{Dt} + \delta_{ij}\left[\bar{J}_i^e - \frac{D_0 P_{ai}}{Dt}\right]\frac{\partial\bar{f}^\circ}{\partial P_i} + \frac{P_j}{B_j}\frac{\partial\bar{f}^\circ}{\partial q_j} - \frac{P_j}{B_j}\frac{\partial\bar{f}^\circ}{\partial P_i}\frac{\partial P_{ai}}{\partial q_j} . \qquad \text{H.2}$$

As outlined in the text:

$$\frac{D_0 P_{ai}}{Dt} = \bar{J}_i^e - \frac{\delta_{ij}}{n}\frac{\partial p}{\partial q_j}$$

where p is the thermodynamic pressure defined as $p = nkT$. Substituting the above into H.2 gives

$$\mathcal{D}\bar{f}' = \bar{f}^\circ\left\{\frac{D_0 \ln\bar{f}^\circ}{Dt} + \frac{\delta_{ij}}{n}\frac{\partial p}{\partial q_j}\frac{\partial \ln\bar{f}^\circ}{\partial P_i} + \frac{P_j}{B_j}\frac{\partial \ln\bar{f}^\circ}{\partial q_j} - \frac{P_j}{B_j}\frac{\partial \ln\bar{f}^\circ}{\partial P_i}\frac{\partial P_{ai}}{\partial q_j}\right\} . \qquad \text{H.3}$$

Since,

$$\bar{f}^\circ = n\prod_{i=1}^{5}(2\pi B_i kT)^{-1/2} e^{-P_i^2/2B_i kT}$$

then:

$$\ln\bar{f}^\circ = \text{constant} + \ln\left[n T^{-5/2}\right] - P_{ii}^2/2B_i kT \qquad \text{H.4}$$

Thus,

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$$\frac{\partial \ln \bar{f}^{\,o}}{\partial P_i} = \frac{-P_i}{B_i kT} \qquad \text{H.5}$$

and

$$\frac{D_o \ln \bar{f}^{\,o}}{Dt} = \frac{D_o \ln\left|nT^{-5/2}\right|}{Dt} + \frac{D_o}{Dt}\left[\frac{-P_{ii}^2}{2B_i kT}\right] \qquad \text{H.6}$$

$$= \frac{T^{5/2}}{n} \frac{D_o}{Dt}\left[nT^{-5/2}\right] + \frac{D_o}{Dt}\left[\frac{-P_{ii}^2}{2B_i kT}\right] \qquad \text{H.7}$$

Expanding the first right-hand term:

$$\frac{D_o}{Dt}\left[nT^{-5/2}\right] = T^{-5/2}\frac{D_o n}{Dt} + n\frac{D_o T^{-5/2}}{Dt} \qquad \text{H.8}$$

and substituting for $\dfrac{D_o n}{Dt}$ from the development of the text yields:

$$\frac{D_o}{Dt}\left[nT^{-5/2}\right] = T^{-5/2}\left\{-n\frac{\partial}{\partial_{1j}}\left[\frac{P_{oj}}{B_j}\right] + n\left(\frac{-5}{2}T^{-7/2}\right)\frac{D_o T}{Dt}\right\} \qquad \text{H.9}$$

Substituting for $\dfrac{D_o T}{Dt}$ from the text gives

$$\frac{D_o}{Dt}\left[nT^{-5/2}\right] = nT^{-5/2}\left\{\frac{-\partial}{\partial_{1j}}\left[\frac{P_{oj}}{B_j}\right] - \left(\frac{5}{2T}\right)\left(\frac{-2T}{5}\right)\frac{\partial}{\partial_{1j}}\left[\frac{P_{oj}}{B_j}\right]\right\} = 0 \qquad \text{H.10}$$

To the first approximation then, the variation of temperature during the motion of the gas follows the adiabatic law:

$$n \propto T^{5/2} \qquad \text{H.11}$$

which implies

$$\frac{5}{2} = \frac{1}{\gamma - 1} \quad ; \quad \gamma = 1.400 \qquad \text{H.12}$$

Equation H.7 becomes then:

$$\frac{D_0 \ln \bar{f}^{\circ}}{Dt} = \frac{D_0}{Dt}\left[\frac{-P_{ii}^2}{2B_i kT}\right] . \qquad \text{H.13}$$

Since $P_i \neq P_i(t)$, then:

$$\frac{D_0 \ln \bar{f}^{\circ}}{Dt} = \frac{-P_{ii}^2}{2B_i k}\frac{D_0 T^{-1}}{Dt} = \frac{P_{ii}^2}{2B_i kT^2}\frac{D_0 T}{Dt} . \qquad \text{H.14}$$

Substituting for $\frac{D_0 T}{Dt}$ yields:

$$\frac{D_0 \ln \bar{f}^{\circ}}{Dt} = \frac{-P_{ii}^2}{5B_i kT}\frac{\partial}{\partial q_j}\left[\frac{P_{0i}}{B_j}\right] . \qquad \text{H.15}$$

The sum of the first and last terms of equation H.3 is:

$$\frac{1}{B_i kT}\left[\frac{P_i P_j}{B_j} - \frac{P_{ii}^2 \delta_{ij}}{5 B_j}\right]\frac{\partial P_{0i}}{\partial q_j} . \qquad \text{H.16}$$

The bracketted term is a non-divergent tensor which shall be designated as $\overset{\bullet}{P_i}P_j/B_j$. Thus, the above equation becomes:

$$\frac{1}{B_i kT}\left[\frac{\overset{\bullet}{P_i}P_j}{B_j}\right]\frac{\partial P_{0i}}{\partial q_j} \qquad \text{H.17}$$

The second and third terms of equation H.3 are:

$$\frac{\delta_{ij}}{n}\frac{\partial P}{\partial q_j}\frac{\partial \ln \bar{f}^{\circ}}{\partial P_i} + \frac{P_j}{B_j}\frac{\partial \ln \bar{f}^{\circ}}{\partial q_j} = \frac{-1}{nkT}\frac{P_j}{B_j}\frac{\partial P}{\partial q_j} + \frac{P_j}{B_j}\frac{\partial \ln \bar{f}^{\circ}}{\partial q_j} \qquad \text{H.18}$$

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which by the definition of the thermodynamic pressure is:

$$= \frac{P_j}{B_j}\left[\frac{\partial \ln \bar{f}^{\circ}}{\partial q_j} - \frac{1}{nkT}\frac{\partial (nkT)}{\partial q_j}\right] \qquad \text{H.19}$$

$$= \frac{P_j}{B_j}\frac{\partial}{\partial q_j}\left[\ln\left|\bar{f}^{\circ}/nkT\right|\right]. \qquad \text{H.20}$$

The bracketted term is:

$$\ln\left|\bar{f}^{\circ}/nkT\right| = \text{constant} + \ln\left|T^{-7/2}\right| - P_{ii}^2/2B_i kT \qquad \text{H.21}$$

which upon substitution into equation H.20 yields

$$\frac{P_j}{B_j}\frac{\partial}{\partial q_j}\left[\ln\left|\bar{f}^{\circ}/nkT\right|\right] = \frac{P_j}{B_j}\left[\frac{\partial}{\partial q_j}\left[\ln\left|T^{-7/2}\right|\right] + \frac{P_{ii}^2}{2B_i kT^2}\frac{\partial T}{\partial q_j}\right] \qquad \text{H.22}$$

$$= \frac{P_j}{B_j}\left[\frac{P_{ii}^2}{2B_i kT^2}\frac{\partial T}{\partial q_j} - \frac{7}{2}\cdot\frac{\partial \ln T}{\partial q_j}\right] \qquad \text{H.23}$$

$$= \frac{P_j}{B_j}\left[\left(\frac{P_{ii}^2}{2B_i kT} - \frac{7}{2}\right)\frac{\partial \ln T}{\partial q_j}\right] \qquad \text{H.24}$$

Equation H.3 is thus:

$$\partial \bar{f}^{\prime} = \bar{f}^{\circ}\left\{\frac{P_j}{B_j}\left[\left(\frac{P_{ii}^2}{2B_i kT} - \frac{7}{2}\right)\frac{\partial \ln T}{\partial q_j}\right] + \frac{1}{B_i kT}\left[\frac{P_i^{\circ}P_j}{B_j}\right]\frac{\partial P_{oi}}{\partial q_j}\right\} \qquad \text{H.25}$$

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By Enskog's solution method:

$$\mathcal{D}' + \mathbb{J}' = 0 .$$

Thus:

$$n^2 \mathbb{I}(\bar{\Phi}') = -\bar{f}^\circ \left\{ \frac{P_j}{B_j} \left(\frac{P_{ii}^2}{2 B_i kT} - \frac{1}{2} \right) \frac{\partial \ln T}{\partial q_j} + \frac{1}{B_i kT} \left[\frac{P_i^\circ P_j}{B_j} \right] \frac{\partial p_{\bullet i}}{\partial q_j} \right\} \qquad \text{H.26}$$

Following Chapman and Cowling[1], the peculiar momentum shall be non-dimensionalized to the reduced momentum. The reduced momentum is defined as:

$$\mathcal{P}_j = \left(\frac{1}{2 B_j kT} \right)^{1/2} P_j \qquad \text{H.27}$$

Defined in terms of the reduced momentum, the equilibrium distribution function is:

$$\bar{f}^\circ = n \prod_{i=1}^{s} (2\pi B_i kT)^{-1/2} e^{-\mathcal{P}_i^2} \qquad \text{H.28}$$

while equation H.26 is:

$$n^2 \mathbb{I}(\bar{\Phi}') = -\bar{f}^\circ \left\{ \left(\frac{2 kT}{B_j} \right)^{1/2} (\mathcal{P}_{ii}^2 - 7/2) \frac{\partial \ln T}{\partial q_j} \mathcal{P}_j + 2 \left(\frac{B_j}{B_i} \right)^{1/2} \left[\frac{\mathcal{P}_i^\circ \mathcal{P}_j}{B_j} \right] \frac{\partial p_{\bullet i}}{\partial q_j} \right\} \qquad \text{H.29}$$

Let us initially define $\bar{\Phi}'$:

$$\bar{\Phi}' = \frac{-1}{n} \left[\mathbb{J}_j \frac{\partial \ln T}{\partial q_j} + k_{ij} \frac{\partial p_{\bullet i}}{\partial q_j} \right] \qquad \text{H.30}$$

such that

$$_n I(\mathbb{J}_j) = \bar{f}^\circ \left(\frac{2kT}{B_j}\right)^{1/2} \left(\mathcal{P}_{ii}^2 - \frac{7}{2}\right) \mathcal{P}_j$$

<div align="right">H.31</div>

$$_n \bar{I}(k_{ij}) = \bar{f}^\circ \, 2 \left(\frac{B_j}{B_i}\right)^{1/2} \left[\frac{P_i^\circ P_j}{B_j}\right] .$$

<div align="right">H.32</div>

Now:

$$\int \bar{f}' \, \gamma^\ell d\vec{P} = \int \bar{f}^\circ \, \bar{\mathfrak{I}}' \, \gamma^\ell d\vec{P}$$

<div align="right">H.33</div>

$$= \frac{\partial l_n \bar{T}}{\partial_j} \int \bar{f}^\circ (\mathcal{P}_{ii}^2 - \frac{7}{2}) \mathcal{P}_j \left(\frac{2kT}{B_j}\right)^{1/2} \gamma^\ell d\vec{P} + 2 \left(\frac{B_j}{B_i}\right)^{1/2} \int \bar{f}^\circ \left[\frac{P_i^\circ P_j}{B_j}\right] \gamma^\ell d\vec{P}$$

<div align="right">H.34</div>

<div align="center">for l = 1,4,5</div>

when l = 1,4,5 because the above is evaluated at a point in
space. The second integral is zero for all Ψ^l because the
integrand is either an odd function of $\vec{P}$ or it is a non-divergent
tensor. For Ψ^1 and Ψ^4 the first integral vanishes because the
integrand is an odd function of $\vec{P}$. For Ψ^5, the first integral
may be recast as:

$$A \int_0^\infty e^{-x^2} (x^2 - \frac{7}{2}) x^6 dx$$

<div align="right">H.35</div>

where A is a constant. The solution of H.35 is:

$$A \left[\Gamma(\frac{9}{2}) - \frac{7}{2} \Gamma(\frac{7}{2})\right] = 0$$

<div align="right">H.36</div>

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Thus, the conditions of solvability for the Enskog method are satisfied. Therefore, since the general solution is the sum of the particular solution and the homogeneous solution:

$$\bar{\Phi}' = -\frac{1}{n}\left\{ J_j \frac{\partial \ln T}{\partial q_j} + k_{ij}\frac{\partial p_{oi}}{\partial q_j}\right\} + \beta^{1,1} + \beta_m^{2,1} p_m + \beta_k^{3,1} \alpha_i p_i + \beta^{4,1} p_{ii}^2/2B_i \qquad \text{H.37}$$

where $\beta^{2,1}$ is a three vector and $\beta^{3,1}$ is a five-vector where:

$$\alpha_i = \epsilon_{ijk} r_j \qquad \text{for } i,j,k = 1 \to 3 \qquad \text{H.38}$$

$$\alpha_i = \hat{e}_i \qquad \text{for } i = 4,5$$

By identity, we may define

$$\beta_i^{5,1} = \epsilon_{jki} \beta_j^{3,1} r_k \qquad \text{for } i,j,k = 1 \to 3 \qquad \text{H.39}$$

$$\beta_i^{5,1} = \beta_i^{3,1} \qquad \text{for } i = 4,5$$

Thus,

$$\bar{\Phi}' = -\frac{1}{n}\left\{ J_j \frac{\partial \ln T}{\partial q_j} + k_{ij}\frac{\partial p_{oi}}{\partial q_j}\right\} + \beta^{1,1} + \beta_m^{2,1} p_m + \beta_i^{5,1} p_i + \beta^{4,1} p_{ii}^2/2B_i \qquad \text{H.40}$$
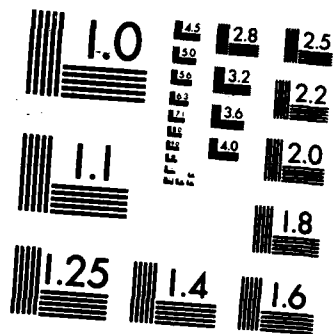
Since equations H.31 and H.32 are functions of $\vec{P}$, n, and T only, then by arguments similar to those of Chapman and Cowling[1]:

$$J_j = J(P)P_j \left(\frac{2kT}{B_j}\right)^{1/2} \qquad \text{H.41}$$

$$k_{ij} = k(P)\left[\frac{P_i^o P_j}{B_j}\right]\left(\frac{B_j}{B_i}\right)^{1/2} \qquad \text{H.42}$$

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where $J(\varphi)$ and $K(\varphi)$ are scalar functions of φ, n, and T. To satisfy the requirement that the average molecular quantities be solely related to f , we must set:

$$\int \psi^i \bar{\underline{I}}' \bar{f}^o \, d\vec{p} = 0 \qquad\qquad \text{H.43}$$

$$\text{for } i = 1,4,5$$

Thus, neglecting vanishing integrals yields

$$i = 1 \qquad \int \bar{f}^o \left(\beta^{1,1} + \beta^{4,1} p_{ii}^2/2B_i \right) d\vec{p} = 0 \qquad\qquad \text{H.44}$$

$$i = 4 \qquad \int \bar{f}^o \left(\beta^{1,1} + \beta^{4,1} p_{ii}^2/2B_i \right) \frac{p_{ii}^2}{2B_i} \, d\vec{p} = 0 \qquad\qquad \text{H.45}$$

$$i = 5 \qquad \int \bar{f}^o \left\{ \frac{-\underline{I}(\varphi)}{n} \left(\frac{2kT}{B_i} \right)^{1/2} \frac{\partial \ln T}{\partial q_{ji}} + \beta_j^{2,1} + \beta_j^{5,1} \right\} p_{ii}^2 \, d\vec{p} = 0 \qquad \text{H.46}$$

Equations H.44 and H.45 imply that $\beta^{1,1}$ and $\beta^{4,1}$ are both zero. Equation H.46 implies that $\beta_j^{2,1}$ and $\beta_j^{5,1}$ are equal and opposite in magnitude for j = 1,2,3. For j = 4,5 , $\beta_j^{5,1} + \hat{e}_j \beta_j^{3,1}$ and therefore

$$\beta_j^{5,1} p_{ii}^2 \qquad \text{for } i = 1 \to 5; \ j = 4,5$$

is proportional to T and can be incorporated into the first term of the integrand of H.46. Thus, we may write:

$$\int \bar{f}^o \left\{ J(\varphi) \varphi_{ii}^2 \right\} d\vec{p} = 0 \qquad\qquad \text{H.47}$$

and

$$\underline{I}' = -\frac{1}{n} \left\{ \left(\frac{2kT}{B_j} \right)^{1/2} J(\varphi)\varphi_j \frac{\partial \ln T}{\partial q_{ji}} + \left(\frac{B_j}{B_i} \right)^{1/2} k(\varphi) \left[\frac{\varphi_i^o \varphi_j}{B_j} \right] \frac{\partial p_{ii}}{\partial q_{ji}} \right\} . \qquad \text{H.48}$$

APPENDIX I
Evaluation of the Thermal Flux Five Vector
and the Stress Tensor

Thermal Flux Vector:

By definition:

$$Q_j' = \int \bar{f}' \left[\frac{P_j P_{ii}^2}{2 B_j B_i} \right] d\vec{p} \qquad \text{I.1}$$

Substituting for $\bar{f}'$:

$$Q_j' = -\frac{1}{n} \int \bar{f}^\circ \left[\left(\frac{2kT}{B_j} \right)^{1/2} J(P) P_j \frac{d\ln T}{dq_j} + \left(\frac{B_j}{B_i} \right)^{1/2} k(P) \left[\frac{P_i^\circ P_j}{B_j} \right] \frac{d P_{ni}}{dq_j} \right] \left[\frac{P_j P_{ii}^2}{2 B_j B_i} \right] d\vec{p} \qquad \text{I.2}$$

$$= -\frac{1}{n} \left(\frac{2kT}{B_j} \right)^{1/2} \int \bar{f}^\circ J(P) P_j \left[\frac{P_j P_i}{2 B_j B_i} \right] \frac{d\ln T}{dq_j} d\vec{p} \qquad \text{I.3}$$

because the integrals of odd functions of $\vec{p}$ vanish. Substituting P_i for P_i yields

$$Q_j' = -\frac{1}{n} \left(\frac{2k^2 T^2}{B_j} \right) \int \bar{f}^\circ J(P) P_i P_j P_{ii}^2 \frac{d\ln T}{dq_j} d\vec{p}. \qquad \text{I.4}$$

Equation I.4 may be simplified using the results of Appendix D:

$$Q_j' = \frac{-2k^2 T^2}{5 n B_j} \frac{d\ln T}{dq_j} \int \bar{f}^\circ P^4 J(P) d\vec{p} \qquad \text{I.5}$$

$$Q_j' = \frac{-2k^2 T}{5 n B_j} \frac{dT}{dq_j} \int \bar{f}^\circ P^4 J(P) d\vec{p} \qquad \text{I.6}$$

or

$$Q_j' = \frac{-\lambda}{B_j} \frac{dT}{dq_j} \qquad \text{I.7}$$

where

$$\lambda = \frac{2k^2 T}{5 n} \int \bar{f}^\circ P^4 J(P) d\vec{p} \qquad \text{I.8}$$

The Stress Tensor

By definition:

$$\tau_{ij}' = \int \bar{f}^\circ \bar{\mathbf{I}}' \left[\frac{P_i P_j}{B_j} \right] d\vec{p} \qquad \text{I.9}$$

$$\tau'_{ij} = -\frac{1}{n} \int \bar{f}^\circ \left[\left(\frac{2kT}{B_j} \right)^{1/2} J(\varphi) \varphi_j \frac{\partial \ln T}{\partial q_j} + \left(\frac{B_j}{B_i} \right)^{1/2} k(\varphi) \left[\frac{\varphi_i^\circ \varphi_j}{B_j} \right] \frac{\partial p_{oi}}{\partial q_j} \right] \left[\frac{P_i P_j}{B_j} \right] d\bar{p} \qquad \text{I.10}$$

$$= -\frac{1}{n} \int \bar{f}^\circ \left(\frac{B_j}{B_i} \right)^{1/2} k(\varphi) \left[\frac{\varphi_i^\circ \varphi_j}{B_j} \right] \frac{\partial p_{oi}}{\partial q_j} \left[\frac{P_i P_j}{B_j} \right] d\bar{p} \qquad \text{I.11}$$

by neglecting vanishing integrals. Substituting for P_i, equation I.11 is equivalent to:

$$\tau'_{ij} = \frac{-2kT}{nB_j} \int \bar{f}^\circ k(\varphi) [\varphi_i^\circ \varphi_j] [\varphi_i^\circ \varphi_j] \frac{\partial p_{oi}}{\partial q_j} d\bar{p} \qquad \text{I.12}$$

From the results of Appendix C, equation I.12 is:

$$\tau'_{ij} = \frac{-2kT}{4nB_j} \frac{\partial p_{oi}^{\circ\circ}}{\partial q_j} \int \bar{f}^\circ k(\varphi) [\varphi_i^\circ \varphi_j] [\varphi_i^\circ \varphi_j] d\bar{p} \qquad \text{I.13}$$

which by equation H.42 is

$$\tau'_{ij} = \frac{-kT}{7n} \left(\frac{B_i}{B_j} \right)^{1/2} \frac{\partial p_{oi}^{\circ\circ}}{\partial q_j} \int \bar{f}^\circ k_{ij} \varphi_i^\circ \varphi_j \, d\bar{p} \qquad \text{I.14}$$

$$= \frac{-kT}{14} \left(\frac{B_i}{B_j} \right)^{1/2} \frac{\partial p_{oi}^{\circ\circ}}{\partial q_j} \int k_{ij} I(k_{ij}) \, d\bar{p} \qquad \text{I.15}$$

In the notation of Chapman and Cowling[1]:

$$\tau'_{ij} = \frac{-kT}{14} \left(\frac{B_i}{B_j} \right)^{1/2} \frac{\partial p_{oi}^{\circ\circ}}{\partial q_j} [k_{ij}, k_{ij}] \qquad \text{I.16}$$

or

$$\tau'_{ij} = -2\mu \left(\frac{B_i}{B_j} \right)^{1/2} \frac{\partial p_{oi}^{\circ\circ}}{\partial q_j} \qquad \text{I.17}$$

where:

$$\mu = \frac{kT}{28} [k_{ij}, k_{ij}] \qquad \text{I.18}$$

Since the stress tensor has been defined as

$$\tau_{ij} = \sum_{i=0}^{\infty} \tau_{ij}^r$$

we have for the second approximation:

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$$\tau_{ij} = p\delta_{ij} - 2\mu\left(\frac{\beta_i}{\beta_j}\right)^{1/2}\frac{\partial \bar{p}_{oi}}{\partial q_j} \qquad \text{I.19}$$

APPENDIX J

Evaluation of the Coefficient of Thermal Conductivity
and the Coefficient of Viscosity

We have for λ:

$$\lambda = \frac{2k^2 T}{5n} \int \bar{f}^\circ \rho^4 J(\rho) \, d\vec{p} \qquad \text{J.1}$$

A linear combination of equations J.1 and H.47 yields:

$$\lambda = \frac{2k^2 T}{5n} \int \bar{f}^\circ \rho_i J(\rho)(\rho_{ii}^2 - \frac{7}{2})\rho_i \, d\vec{p} \qquad \text{J.2}$$

which by equation H.31 is equivalent to:

$$\lambda = \frac{2k^2 T}{5} \int J_i I(J_i) \, d\vec{p} \qquad \text{J.3}$$

Summarizing for a moment, the coefficients of heat conductivity and viscosity for a gas composed of rigid-rotors are:

$$\lambda = \frac{2k^2 T}{5} \int J_i I(J_i) \, d\vec{p} \quad ; \quad \mu = \frac{kT}{2\beta} \int k_{ij} I(k_{ij}) \, d\vec{p}.$$

The application of Sonine polynomials to the above integrals is very similar to their application in the case of a monatomic gas. Thus, only the minor arithmetic changes are noted below. The derivation again closely follows that of Chapman and Cowling[1].

From equation J.2, $\alpha_0 = 0$ and

$$\alpha_r = \frac{1}{n} \int \bar{f}^\circ (\rho^2 - \frac{7}{2}) S_{9/2}^{(r)}(\rho^2) \rho^2 \, d\vec{p} \qquad \text{J.4}$$

where the subscripts on ρ have been deleted for notational ease since:

$$S_{9/2}^{(1)}(\rho^2) = \frac{7}{2} - \rho^2$$

we have:

$$\alpha_r = \frac{-1}{n} \int \bar{f}^\circ S_{9/2}^{(1)}(\rho^2) S_{9/2}^{(r)}(\rho^2) \rho^2 \, d\vec{p} \qquad \text{J.5}$$

$$= \frac{-1}{\pi^{3/2}} \int e^{-\rho^2} S_{9/2}^{(1)}(\rho^2) S_{9/2}^{(r)}(\rho^2) \rho^2 \, d\vec{\rho} \qquad \text{J.6}$$

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The results of Appendix C lead to:

$$\alpha_r = \frac{-8}{3\pi^{1/2}} \int_0^\infty e^{-P^2} S_{5/2}^{(1)}(P^2) S_{5/2}^{(r)}(P^2) P^6 dP \qquad \text{J.7}$$

$$= \frac{-4}{3\pi^{1/2}} \int_0^\infty e^{-P^2} S_{5/2}^{(1)}(P^2) S_{5/2}^{(r)}(P^2) P^5 d(P^2) \qquad \text{J.8}$$

$$\alpha_r = \frac{-4\Gamma(9/2)}{3\pi^{1/2}} = \frac{-35}{4} \quad \text{for} \quad r=1 \qquad \text{J.9}$$

$$= 0 \quad \text{for} \quad r > 1$$

Thus:

$$\int J_j \bar{I}(J_j) d\vec{P} = \frac{(35)^2}{16} \left[\frac{1}{a_{11}} + \frac{(A_{12}^{(2)})^2}{A^{(1)}A^{(2)}} + \frac{(A_{13}^{(2)})^2}{A^{(2)}A^{(3)}} + \cdots \right] \qquad \text{J.10}$$

and

$$\lambda = \frac{245}{8} k^2 T \left[\frac{1}{a_{11}} + \frac{(A_{12}^{(2)})^2}{A^{(1)}A^{(2)}} + \cdots \right] \qquad \text{J.11}$$

Likewise, the development of

$$\int k_{ij} \bar{I}(k_{ij}) d\vec{P}$$

begins with:

$$\beta_r = \frac{8}{5n} \int \bar{F}^o S_{7/2}^{(r-1)}(P^2) P^4 d\vec{P} \qquad \text{J.12}$$

which leads to:

$$\beta_r = \frac{8}{5\pi^{3/2}} \int e^{-P^2} S_{7/2}^{(0)}(P^2) S_{7/2}^{(r-1)}(P^2) P^4 d\vec{P} \qquad \text{J.13}$$

$$= \frac{64}{15\pi^{1/2}} \int_0^\infty e^{-P^2} S_{7/2}^{(0)}(P^2) S_{7/2}^{(r-1)}(P^2) P^8 dP \qquad \text{J.14}$$

$$= \frac{32}{15\pi^{1/2}} \int_0^\infty e^{-P^2} S_{7/2}^{(0)}(P^2) S_{7/2}^{(r-1)}(P^2) P^7 d(P^2) \qquad \text{J.15}$$

$$\beta_r = \frac{32 \Gamma(9/2)}{15 \pi^{1/2}} = 14 \quad \text{for} \quad r=1 \qquad \text{J.16}$$

$$\beta_r = 0 \quad \text{for} \quad r > 1$$

Thus:

$$\int k_{ij} \bar{I}(k_{ij}) d\vec{P} = (14)^2 \left[\frac{1}{b_{11}} + \frac{(B_{12}^{(2)})^2}{B^{(1)}B^{(2)}} + \frac{(B_{13}^{(2)})^2}{B^{(2)}B^{(3)}} \right] \qquad \text{J.17}$$

and

$$\mu = \left(\frac{kT}{2\xi}\right)(\eta)^2 \left[\frac{1}{b_{11}} + \frac{\left(B_{12}^{(2)}\right)^2}{B^{(1)}B^{(2)}} + \cdots\right] \qquad \text{J.18}$$

$$\mu = 7kT \left[\frac{1}{b_{11}} + \frac{\left(B_{12}^{(2)}\right)^2}{B^{(1)}B^{(2)}} + \cdots\right] \qquad \text{J.19}$$

Lastly, the Prandtl number is defined as:

$$P_r = \frac{\mu C_p}{\lambda} \qquad \text{J.20}$$

For a diatomic gas molecule, $C_p = 3.5k$. Substituting this into the above along with equations J.11 and J.19 yields

$$P_r = \frac{4a_{11}}{5b_{11}} \qquad \text{J.21}$$

where the higher order terms of the Sonine polynomials have been neglected.

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